

ANALYTICAL ABSTRACTS

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

625. Examples of analysis by activation. P. Leveque (Commissariat à l'Energie Atomique, Boite Postale No. 2, Gif sur Yvette, S. et O., France). *Rapp. Cent. Et. Nucl. Saclay*, 1955, No. 423, 6 pp.—The principles and techniques of analysis by neutron and X-ray activation are outlined and their application to the determination of rare earths, O, Hf and F is briefly described. (17 references.) S.C.I. ABSTR.

626. Resorcyldoxime as an organic reagent. Ajit Kumar Mukherjee (Indian Ass. Cultivation Sci., Calcutta, India). *Anal. Chim. Acta*, 1955, **13** (4), 334–339.— β -Resorcyldoxime reacts with Cu^{++} to give a greenish-grey ppt., $\text{Cu}(\text{C}_6\text{H}_3\text{O}_3\text{N})_2$, and the reaction detects 1 pt. of Cu in 40,000 pt. of soln. The reagent can also be used gravimetrically, but a large excess (6 to 7 times by wt.) must be added to ensure complete pptn. *Procedure*—To 125 ml of soln., containing 0.005 to 0.036 g of Cu^{++} , add 20 to 25 ml of 1 per cent. aq. β -resorcyldoxime, and adjust the pH to between 1.8 and 2.85. Warm slightly on a water bath, set aside for 0.5 to 1 hr., filter in a Gooch crucible and wash with cold water. Dry at 100° to 105°C and weigh. 1 g of ppt. \equiv 0.1729 g of Cu. The method is applied to the determination of Cu in brass and in the presence of Cd^{++} , Zn^{++} , Pb^{++} or Co^{++} . Nickel, which yields a similar complex, can be detected by an opalescence at a concn. of 1 in 200,000 and gives a colour at a concn. of 0.25 p.p.m. It can be determined gravimetrically in the presence of Cd^{++} , Co^{++} , Zn^{++} or Pb^{++} by a procedure similar to that for Cu, but the pH is adjusted to between 5.30 and 6.15. Although Cu is pptd. from more acid soln. than is Ni it cannot be separated quant. by this means. A ppt. is given by Mn^{++} at pH 8.6 and by Hg^{++} at pH 6.5; Co^{++} give a red colour at pH > 7.5 and UO_2^{++} an orange colour at pH > 8 . W. C. JOHNSON

627. Sodium naphthionate, a reagent for the detection and quantitative determination of nitrites. K. H. Boltze and H. Katzmann (Friedrich Schiller Univ., Jena, Germany). *Pharm. Zentralh.*, 1955, **94** (5), 175–177.—To 1 ml of test solution containing nitrite (1 to 40 μg) in 0.01 N HCl add immediately a solution of Na naphthionate (0.1 per cent.) (3 ml). The extinction of the red-orange azo dye reaches its maximum value after 1 hr. and remains stable for about 3 hr. Excess of Na naphthionate does not interfere and Beer's law is obeyed for concn. of nitrite of 0.5 to 40 μg per ml. The useful range can be extended by the use of cells with a light path > 1 cm. P. S. STROSS

628. New substituted 1:10-phenanthrolines as ferroine- and cuproine-reacting ligands. D. H. Wilkins, A. A. Schilt and G. F. Smith (Univ. Illinois, Urbana, Ill., U.S.A.). *Anal. Chem.*, 1955, **27** (10),

1574–1575.—Eleven new substituted 1:10-phenanthrolines have been synthesised; the wavelengths of max. absorption and the mol. extinction coeff. of their Fe^{II} and Cu^I complexes are listed. The substituents replacing hydrogen in the 4- and 5- and the 2:9-, 4:7- and 5:6-positions are compared as electron donors. For 4:7-substitution the order of magnitude of electron donation is methoxy $<$ phenoxy $<$ ethyl $<$ phenyl, whilst for the same substituent, electron donation is greater in the ferroine than in the cuproine chelation.

W. J. BAKER

629. Precipitation from homogeneous solution. J. 'Agterdenbos (Lab. Anal. Chem., Amsterdam, Holland). *Chem. Weekbl.*, 1955, **51** (32), 571–576.—A survey of pptn. methods, where local supersaturation of reagent is avoided, is given, their application to gravimetric analysis is described and their advantages are critically discussed. The various methods used to achieve gradual change of pH value in hydroxide and other pptn., the formation of pptg. anions by ester hydrolysis *in situ*, and sulphide formation by decomposition of organic thio compounds, etc., are given. (74 references.) H. A. FISHER

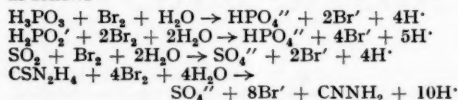
630. Ascorbic acid as a reducing agent in quantitative analysis. I. G. Gopala Rao and V. Narayana Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1955, **147** (5), 338–347.—The stability of ascorbic acid soln. is greater at higher concn. than at lower concn. Slight acidification helps considerably to protect the soln., whilst saturation with CO_2 and preservation in an atm. of CO_2 are further aids to stability. The addition of oxalic acid is also effective; whether in air or in CO_2 . As an example of the stability of ascorbic acid soln. in CO_2 , a 0.066 N soln. acidified to 0.04 N with H_2SO_4 shows only 0.6 per cent. deterioration in 4 days, whilst soln. of a similar concn. are fairly stable (≈ 1.4 per cent. deterioration) for more than a week without the addition of acid. J. H. WATON

631. The use of complexones in volumetric analysis. H. Flaschka. *Fortschr. Chem. Forsch.*, 1955, **3**, 253–308.—A review with 183 references is given. N. E.

632. 4-Aminopyridine as standard in acidimetry. C. E. Van Hall and K. G. Stone (Mich. State Univ., East Lansing, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1580–1582.—4-Aminopyridine has a dissociation constant of 1.3×10^{-5} and may be used as a standard with either 0.1 N or 0.5 N acid, and methyl orange as indicator. The free base is purified by recrystallisation from toluene or benzene and is easily recovered after use. Standardisation of acids with this base yields normalities within 1 part per 1000 of those obtained with Na_2CO_3 .

G. P. COOK

633. Bromine-acidimetric methods. IX. L. Rosenthaler (Seftigenstrasse 40, Berne, Switzerland). *Pharm. Acta Helv.*, 1955, **30** (8), 332-335.—The assay of phosphorous acid, sodium hypophosphite, sulphurous acid and thiourea is described. The sample is oxidised with bromine and the acid formed is titrated with NaOH. The reactions are as follows—



The determination takes from 10 to 30 minutes.

P. S. STROSS

634. Hydrazinometry, a new type of reductimetric titration. J. Zýka and J. Vulterin (Karlovy Univ., Prague). *Coll. Czech. Chem. Commun.*, 1955, **20** (4), 804-809.—A 0.1 M soln. of hydrazine sulphate can be prepared directly from the pure solid. The soln. is stable, and gives good results for the titration of BrO_3^- , IO_3^- , IO_4^- , I^- , $[\text{Fe}(\text{CN})_6]^{3-}$, MnO_4^- , Au^{III} and active chlorine. The end-points of the titrations can be detected visually or potentiometrically.

J. H. WATON

635. Fluorescent indicators. F. Dangel (College Agric., Vienna). *Prakt. Chem.*, 1955, **6** (9), 249.—A table is given of 23 substances which in aq. solution fluoresce under u.v. light with a colour or intensity dependent on the pH, and are therefore useful for titrating strongly coloured liquids. The pH range 0 to 14 is covered. The colour change and a literature reference for each substance are given. (26 references.)

A. R. PEARSON

636. Effect of temperature of injection upon the separation of liquid mixtures by gas-phase chromatography. F. H. Pollard and C. J. Hardy (Bristol Univ., England). *Chem. & Ind.*, 1955, (37), 1145-1146.—The method of injection of gas and liquid samples on to gas-chromatographic columns (Ray, *Anal. Abstr.*, 1954, **1**, 995) was studied in respect of the effect of variations of injection temp. (I) on peak height (II) and theoretical plate number (III). Mixtures of various org. liquids were injected in various amounts at various temp. on a Kieselguhr column (80 cm \times 4 mm internal diam.), carrying 2 g of dinonyl phthalate at 40° C. For acetone and CH_2Cl_2 in a mixture (equal parts by vol.) of these with CHCl_3 and CCl_4 , the variation of II and III with I was greater at room temp. than at temp. > 50° C and this effect became more pronounced with increase in the vol. of sample injected. Comparison of II for each component of a mixture with II for an internal standard is also shown.

S.C.I. ABSTR.

637. The selectivity of the stationary liquid in vapour-phase chromatography. A. I. M. Keulemans, A. Kwantes and P. Zaai (Koninklijke Shell-Laboratorium, Amsterdam, Netherlands). *Anal. Chim. Acta*, 1955, **13** (4), 357-372.—The theory of vapour-phase chromatography is discussed from a fundamental standpoint. The importance of selecting suitable stationary liquids is illustrated by an account of a number of experiments. These experiments are concerned with the separation of (a) C_4 -hydrocarbon gases, saturated and unsaturated, (b) saturated hydrocarbons from aromatic substances, and (c) the mixture of substances obtained in the dehydrogenation of isopropyl alcohol to acetone.

W. C. JOHNSON

638. Direct quantitative determinations by paper chromatography. A. Lewandowski. *Roczn. Chem.*, 1955, **29**, 871-875.—The technique of measuring spot areas in quant. paper-chromatographic analyses is discussed. The method is demonstrated with several cations and gives results with an error of 5 per cent. Spots of Ni^{++} , Co^{++} and Cu^{++} (from a mixture) were collected on the same paper (Whatman No. 1) by using butanol-acetone-conc. HCl (20:60:20) as eluent and rubeanic acid as spot indicator. A mixture of butanol, acetone, conc. HNO_3 and H_2O (20:60:10:10) was used to elute Al^{+++} in the presence of Fe^{+++} (on Whatman paper No. 3) and, after determining Al with the aid of the fluorine reaction (against phenolphthalein), spots of Fe were developed with $\text{K}_3\text{Fe}(\text{CN})_6$. Bivalent lead was determined singly (on Munktell paper No. 0), from a solution of PbSO_4 in ammonium acetate, by using a solvent mixture of butanol, ethanol and H_2O (70:20:10) with addition of ammonium acetate and H_2S as indicator.

S.C.I. ABSTR.

639. Vacuum-fusion analysis by the iron-bath technique. W. H. Smith (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1636-1637.—The increased viscosity of the iron bath used in vacuum-fusion analysis (*cf. Anal. Abstr.*, 1956, **3**, 696) is caused by the pptn. of graphite flakes, the bath becoming semi-solid within 2 hr. at 1800° C. Solidification starts at the surface. A theory for the effect is proposed.

W. J. BAKER

640. Radioactive tracing. VI. Radio-isotopes as an analytical tool. F. P. W. Winteringham (Pest Infestation Lab., Slough, Bucks., England). *Lab. Practice*, 1955, **4** (8), 328-333.—Advice is given on the planning of radioactive-tracer tests. In the application of radio-isotopes to analysis, there are three methods by which the radio-isotope can be associated with the material to be determined: isotopic dilution, selection reaction with a labelled reagent and radioactivation of the element to be determined. Each of these methods is discussed with the aid of an example.

J. H. WATON

See also Abstract 733.

2.—INORGANIC ANALYSIS

641. Inorganic paper-chromatography. I. Rates of migration of the cations during paper chromatography under different conditions. G. Sommer (Balneol. Inst., Univ. Munich). *Z. anal. Chem.*, 1955, **147** (4), 241-266.—Data are given which show how the R_F values of cations are affected by varying the conditions under which the chromatogram is prepared. For a developing solvent consisting of a mixture of HCl ($d = 1.19$), methanol and water (10:80:10), the effect is studied of the presence of anions, the amount of substance taken, the presence of other cations, the variation of temp., the type of paper used and the age of the developing solvent. The effect of varying the proportion of the components in the solvent is investigated, as well as that of altering the concn. of the HCl, and the substitution of other acid and organic components. Suitable soln. for spraying the chromatograms to reveal the ions are described. In a theoretical discussion it is concluded that the behaviour of the cations during paper chromatography is best explained by an adsorption process.

J. H. WATON

642. Modified technique in [inorganic] chromatography. K. Krishnamurti and B. V. Dhreshwar (College of Science, Nagpur, India). *Research*, 1955, 8, S26.—A chromatographic method is described for separating inorganic radicles into sharp and straight coloured bands. Strips of Whatman filter-paper No. 1, 15 cm \times 1.5 cm, were immersed briefly in a hot agar sol (2 to 4 per cent.) containing reagents that react with the radicles to be tested, drained from excess liquid, and then cooled so that the agar sol, partly impregnating and partly coating the paper, solidified. The prepared paper strip was dipped to a height of 1 mm in the aqueous test solution for 1 to 2 hr. until fine, sharp, and straight coloured bands corresponding to the different radicles appeared. A greater separation of zones, with retention of the straight and sharp appearance, could be effected by adding a suitable quantity of butanol to the test solution before dipping the end of the gel-coated filter-paper into it.

O. M. WHITTON

643. Chromatography of electrolytes on silica gel. F. Umland and K. Kirchner (Inst. Inorg. Chem., Techn. Hochschule, Hanover, Germany). *Z. anorg. Chem.*, 1955, 280, 211-222.—An investigation was made of the adsorption of CuCl_2 on technical silica-gel preparations that contain alkali. Besides an exchange of Na^+ for Cu^{++} , there is an adsorption of Cu^{++} and to a smaller extent of Cl^- . In this way surface compounds are formed, in a manner that resembles the pptn. of hydroxides and basic salts. The pH of the adsorption medium after adsorption is less than that of a pure CuCl_2 soln. of the same concn. When an alkali-free gel is used, no adsorption can be detected, and only a small exchange of cations and anions for H^+ and OH^- takes place. Thus the theory, developed for Al_2O_3 , that the adsorption of electrolytes by inorganic material is primarily due to a H^+ -cation exchange and an OH^- -anion exchange is applicable to silica gel. The much smaller OH^- exchange found for silica gel is due to its acid character.

J. H. WATON

644. Electrophoresis. IX. Separation of cations by means of complex formation with polyphosphates. Masafumi Maki (Japan Women's Univ., Tokyo, Japan). *Japan Analyst*, 1955, 4 (5), 302-304.—A sample soln. containing Ni, Co, Zn, Cu and Cd is mixed with 0.025 M $\text{Na}_2\text{P}_2\text{O}_7$ (or $\text{Na}_4\text{P}_2\text{O}_7$) in a ratio of 1:2 v/v. The pH value of the phosphate soln. is adjusted by adding 2 N HCl. The soln. is spotted on a filter-paper and submitted to electrophoresis (200 V, 4 hr.). In a basic soln., appreciable formation of anionic complexes is observed; all their spots move towards the anode, and show similar mobilities. In a soln. of pH 2, only Ni fails to form an anionic complex, whilst at pH 1.1 every ion migrates towards the cathode. The mobilities of these ions, as well as those of Bi, Pb, Al and Fe, are so different from each other that the separation of spots of Cu, Cd, Bi and Pb, Al, Fe^{+++} and CrO_4^{--} , or Ni, Co and Zn, which is otherwise difficult, can be effected under the given conditions. **X. Separation of cations by means of complex formation with metaphosphate.** Masafumi Maki. *Ibid.*, 1955, 4 (5), 304-307.—A similar experiment was carried out with the use of HPO_3 , $(\text{HPO}_3)_2$ and $(\text{HPO}_3)_3$ in soln. of various pH values (1 to 9). In HPO_3 soln. the ions of Ni, Co, Zn, Cu and Cd form complexes at pH values > 1.7 , whilst in $(\text{HPO}_3)_2$ soln. complexes are formed at pH values > 1.2 . In $(\text{HPO}_3)_3$ complex formation is so marked that even at pH 0.65 the

spots move towards the anode. Separation of spots by paper electrophoresis can be effected in acid soln. containing HPO_3 or $(\text{HPO}_3)_2$ for ions that cannot otherwise be separated, e.g., Fe^{+++} - Al, Zn - Co - Ni, Ca - Ba, Ni - Cu - Fe^{+++} and Ni - Zn - Al.

K. SAITO

645. Volumetric studies in oxidation-reduction reactions. IV. Oxidation with chloramine T. Iodine monochloride method. Balwant Singh and K. C. Sood (Punjab Univ. Coll., Hoshiarpur, India). *Anal. Chim. Acta*, 1955, 13 (4), 301-304.—Chloramine T (**I**) is used to titrate the following substances (the mol. equiv. of **I** is indicated where it differs from unity): KI , N_2H_4 (**2I**), As_2O_3 (**2I**), SnCl_2 , Hg_2Cl_2 , Sb_2O_3 (**2I**), KSCN (**3I**) and FeSO_4 (**0.5 I**). **Procedure**—Dissolve the sample in a mixture of 25 ml of water and 25 ml of conc. HCl and add 5 ml of 0.02 M ICl and 5 ml of CHCl_3 . Titrate with 0.1 N **I** until, after shaking, the aq. layer is pale yellow and the CHCl_3 layer is purple. Continue with smaller additions and vigorous shaking until a colour change to very pale yellow in the CHCl_3 layer indicates the end-point. The HCl concn. must be kept between 4 N and 6 N. **V. Oxidation with chloramine T. Indirect determinations.** Balwant Singh and K. C. Sood. *Ibid.*, 1955, 13 (4), 305-308.—Chloramine T is used for the indirect determination of H_2O_2 , PbO_2 , SeO_2 and Na formate. The reactions involved are similar to those described in *Anal. Abstr.*, 1955, 2, 535. Similarly, KIO_4 is determined by treating it first with 0.1 N As_2O_3 in excess; KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ are treated with 0.1 N $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ in excess. In each method the final titration follows the general procedure described above in Part IV.

W. C. JOHNSON

646. Precipitation of metals with potassium ferrocyanide in presence of complexing agents. K. L. Cheng (Univ. Connecticut, Storrs, Conn., U.S.A.). *Anal. Chem.*, 1955, 27 (10), 1594-1596.—The effect of 5 per cent. soln. of EDTA (disodium salt), $\text{Na}_2\text{S}_2\text{O}_3$ and KF, respectively, on the reactions of more than 30 metal ions with aq. $\text{K}_4\text{Fe}(\text{CN})_6$ is reported. By using these three complexing agents to sequester interfering ions, it is possible to ppt. only Mn or Zn with $\text{K}_4\text{Fe}(\text{CN})_6$ at pH 1 to 3. The sensitivity is 1 μg of Mn at a limiting concn. of 1 in 10^6 and 50 μg of Zn at a limiting concn. of 1 in 2×10^4 . The reaction can also be used for the quant. volumetric determination of Mn with 0.05 M $\text{K}_4\text{Fe}(\text{CN})_6$ at pH 2.3 to 2.5, without previous separation of other metals; the indicator is diphenylamine; Co , MoO_4^{--} and UO_2^{++} interfere. Zinc cannot be determined in this way because it is too strongly complexed by the EDTA, but both Zn and Mn can be determined by high-frequency titration with $\text{K}_4\text{Fe}(\text{CN})_6$ in the presence of EDTA at pH 2.5, the Zn being pptd. first and then the Mn.

W. J. BAKER

647. Quantitative analysis without separation. XVI. Gravimetric analysis without separation for the systems Ba - Mg (oxalates) and Ni - Fe (sulphates). Nobuyuki Unohara. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, 76 (4), 357-359.—The thermal decomposition curves of BaC_2O_4 , MgC_2O_4 , BaC_2O_4 - MgC_2O_4 , NiSO_4 and NiSO_4 - $\text{Fe}_2(\text{SO}_4)_3$ were studied with a thermobalance. The decomposition of $\text{Fe}_2(\text{SO}_4)_3$ ends before NiSO_4 begins to decompose; the determination of Fe (> 15 per cent.) in the mixed sulphates with Ni is effected from the weight difference at 440°C and 685°C .

The determination of both Mg (> 30 per cent.) and Ba (> 20 per cent.) in the mixed oxalates was also made from heating to constant weight at 260° C and 550° C. **XVII. Gravimetric analysis without separation for the systems Fe - Be (sulphates) and Fe - Zn (sulphates).** Nobuyuki Unohara. *Ibid.*, 1955, **76** (4), 359-361.—A similar experiment was carried out with BeSO_4 - $\text{Fe}_2(\text{SO}_4)_3$ and ZnSO_4 - $\text{Fe}_2(\text{SO}_4)_3$. The attempt to determine the amount of Fe in the mixed sulphates with Be or Zn met with little success. **XVIII. Gravimetric analysis without separation for the systems Bi - Cu (sulphates) and Pb - Ba (oxalates).** Nobuyuki Unohara. *Ibid.*, 1955, **76** (6), 615-618.—Thermal decomposition curves were studied similarly with $\text{Bi}_2(\text{SO}_4)_3$ - CuSO_4 , PbC_2O_4 , and PbC_2O_4 - BaC_2O_4 . At 860° C the mixed sulphates are converted into a mixture of $(\text{BiO})_2\text{SO}_4$ and CuO , but constancy in weight is hardly maintained at this temp. The mixed oxalates of Pb and Ba produce a mixture of PbO and BaCO_3 at 480° C and the weight remains constant until 850° C. Both Pb and Ba (> 15 per cent.) can be determined from the difference of weights at 250° C and 550° C. **XIX. Gravimetric analysis without separation for the systems Al - Zn (sulphates) and Bi - Zn - Cd - Pb (sulphates).** Nobuyuki Unohara. *Ibid.*, 1955, **76** (6), 618-620.—Similar experiments were carried out with $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$ - ZnSO_4 , and the mixed sulphates of Bi, Zn and Pb and of Bi, Zn, Cd and Pb. The determination of Al and Zn from the weight difference can be effected only when the amounts of the ingredients are of comparable order. The attempt to determine the amounts of Bi and Zn in the presence of Pb and Cd from the weight difference of the mixed sulphates on heating met with little success. K. SAITO

648. Analysis of a quaternary system of four reciprocal salts. J. B. Bloch and J. Molina. *Afinidad*, 1955, **32**, 91-97.—The Jänecke type of projection for the representation of such a quaternary system is described, with the method of its construction for the system $\text{KCl} + \text{NaNO}_3 \rightleftharpoons \text{NaCl} + \text{KNO}_3$. A modification is described in which the usual Cartesian co-ordinates (perpendicular axes) are replaced by tangential co-ordinates (parallel axes). Greater accuracy of determinations is thus attained. Ionic proportions of Cl^- are determined by titration with NH_4SCN after addition of excess of AgNO_3 ; K is determined gravimetrically as KClO_4 . D. LEIGHTON

649. A quick method of assay of common salt from sea brine. R. L. Desai and K. P. Singh (Centr. Salt Res. Inst., Bhavnagar, India). *J. Sci. Ind. Res. A, India*, 1955, **14** (8), 379-384.—A quick and direct volumetric procedure for the analysis of common salt is described and a number of methods normally used are surveyed briefly. The method now proposed involves the determination of Ca, Mg and sulphate present in the salt by simple volumetric procedures. Chloride is determined volumetrically in the usual manner by Mohr's method. It is assumed that amounts of K, Br and other elements are negligible. Estimation of Ca and Mg is by titration against EDTA. Three procedures are outlined for the estimation of Ca and Mg in the presence of one another. Sulphate estimation is carried out with acidified BaCrO_4 soln. Results are tabulated and discussed for 5 salt samples analysed both by the proposed method and by the usual methods. G. C. JONES

650. The quantitative flame-photometric determination of sodium and potassium in soda-lime glass. F. Hegemann and B. Pfab. *Glastech. Ber.*, 1955, **28** (3), 85-89.—The soda-lime glass is successively treated with HF (10 ml, 40 per cent.) and oxalic acid (0.5 g in 10 ml of water) on a water bath; the excess of oxalic acid is sublimed at 190° C and the K and Na are ultimately dissolved as their oxalates (in 100 ml of water); no appreciable Na or K is retained by the pptd. Ca oxalate. The flame-photometric determination of the Na and K, with oxalate reference solutions, is sensitive to ± 0.05 per cent. of Na_2O and ± 0.04 per cent. of K_2O , affording an accuracy of ± 0.5 per cent. for the content of Na or total alkali. The total time required for parallel determinations of Na and K is about 2 hr. D. R. GLASSON

651. Spectrographic determination of rubidium in plant and animal tissues. B. L. Glendening, D. B. Parrish and W. G. Schrenk (Kansas State College, Manhattan, Kans., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1554-1556.—Rubidium can be determined in plant and animal tissues by using flame excitation and a high-dispersion spectrograph in order to reduce interference from other elements. Interference from K is reduced by means of a mask fitted over the photographic plate so that the K 7664.9 Å and K 7699 Å lines are masked; the analytical Rb line is 7800.2 Å. Concentrations of Rb as low as 1 p.p.m. can be determined. A precision of 1.11 per cent. was attained with rat-liver tissue. The rubidium content of ≈ 40 human foods and animal feeding-stuffs was determined. G. P. COOK

652. The flame-photometric determination of alkalis and calcium in refractory materials by means of a propane flame. F. Reich and F. Grabbe. *TonindustrieZtg.*, 1955, **79**, 127.—With certain adjustments to make it suitable for the use of propane, the flame photometer can be used to determine alkalis in the usual manner. For the determination of Ca the e.m.f. of the photocell must be amplified; the method of doing this is described in detail. The result of the determination of Ca by means of the propane flame is affected by interfering elements to a greater extent than if an acetylene flame is used. Methods of avoiding this interference and the determination procedure are described. A more rapid method for the determination of CaO and MgO is also given. BRIT. CERAM. ABSTR.

653. A rapid determination of copper in converter matte and slag. I. Sasiti Ikeda (Nippon Mining Co., Saganoseki, Oita-ken, Japan). *Japan Analyst.*, 1955, **4** (5), 286-290.—A rapid method (< 10 min.) for the determination of Cu in converter matte (20 to 80 per cent.) and slag (1 to 4 per cent.) for factory control was suggested by the measurement of the extinction at 970 m μ in HNO_3 soln. (0.1 to 1 N). The colour of Fe^{+++} (> 200 mg per 200 ml) is masked by the addition of NaF, which does not affect the absorption of Cu^{++} under the given conditions. A rapid dissolution of the sample is achieved by the use of KClO_3 and HNO_3 . No change in the extinction results from the presence of other metals that are contained in the sample, e.g., Zn, Pb, Ni, Co, Mn, Sn and Sb. *Procedure for matte*—The sample (1 g) is dissolved in HNO_3 (1 + 1) (15 ml) and KClO_3 (4 g), cooled, transferred to a calibrated flask containing a saturated soln. of NaF (10 ml), and made up to 200 ml. The soln.

is filtered through a dry filter-paper and its extinction is measured. The temp. of this soln. is measured at the same time, and the amount of Cu is calculated with the use of a working diagram prepared at the given temp. *Procedure for slag*—The sample (1 g) is heated with HNO_3 (2 + 1) (30 ml) and KClO_3 (4 g) for 4 min., treated with HF (3 ml) and heated for a further 3 min. The product is neutralised with aq. NH_3 soln., made acid with HNO_3 and transferred to a 100-ml calibrated flask together with NH_4F (10 per cent., 5 ml). The soln. is filtered and the extinction is measured as described above.

K. SAITO

654. Colorimetric method of determining silver in photographic emulsions. A. Hulanicki and B. Gluck. *Przem. Chem.*, 1955, **11**, 149.—Quantitative methods available are gravimetric (with an error due to gelatin present), volumetric (oldest and most used), electrolytic (very accurate) and colorimetric. In the last, the absorption of colloidal soln. of Ag_2S is measured in a Pulfrich photometer, with a green filter S57. Gelatin in concn. of 15 to 100 mg has no effect on the absorption of 2.5 to 25 mg of Ag_2S in 250 ml of soln. used, which is equivalent to 15 g of emulsion. Changes of pH also have no effect. Results are accurate to within ± 2.4 per cent. if measurements are made within 30 min.

A. O. JAKUBOVIC

655. Analysis of residues obtained on treatment of ancient base silver alloys with nitric acid. E. R. Caley and C. D. Oviatt (Ohio State Univ., Columbus, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1602-1604.—The two new procedures described for the complete analysis of the residues (Au, AgCl , H_2SnO_3 , Fe_2O_3 and CuO) enable each of these five components to be determined to within ± 2 mg. *Procedure I*—For uncorroded alloys, the residue is ignited at 900°C to const. wt., fused with NH_4I at 475°C and finally ignited at 900°C to const. wt.; the wt. loss = SnO_2 . By leaching with conc. HCl , Fe_2O_3 and CuO are removed (they are added to the main filtrate containing metals sol. in HNO_3), a residue of Au being left (plus SiO_2 , etc.) in the crucible. An accurate value for Au is obtained by dissolution in cold aqua regia, followed by reduction to the metal with oxalic acid. *Procedure II*—For corroded alloys, the residue is ignited in air at $> 500^\circ\text{C}$, cooled and treated with saturated aq. NH_4I , after which the contents of the crucible are filtered. The filtrate contains Ag which, after oxidation of the iodide with conc. H_2SO_4 , can be determined as AgCl . The paper and residue are treated as in procedure I, the original crucible being used. A correction for the solubility of AgCl in NH_4I soln. is applied.

W. J. BAKER

656. Electrometric determination of gold in gold ores. K. A. Murray and G. J. R. Krige. *S. Afr. Ind. Chem.*, 1955, **9** (6), 110-114.—The electrometric titration of 0.01 M AuCl_3 solutions with KI gives sharp end-points, which are unaffected by the presence of chlorides of most metals. The error due to FeCl_3 is eliminated by adding H_3PO_4 . Small concn. of HCl do not affect the result, but the presence of HNO_3 is detrimental. In assaying gold ores, 383.5 g of ground, sieved and quartered ore are digested in bromine water and chlorine water or in aqua regia. The liquid is filtered, evaporated to ≈ 150 ml and titrated with 0.01 M KI. Each ml of 0.01 M KI added corresponds to 1 dwt of Au per ton of ore. The method gives quite good results

but cannot be recommended as a substitute for the conventional fire assay.

A. M. SPRATT

657. The spectrochemical determination of magnesium and beryllium in aluminium alloys using a rotating-disc electrode. N. Haigh (Aluminium Laboratories, Ltd., Banbury, England). *Metalurgia*, 1955, **52**, 154-156.—A spectrochemical method for the analysis of small amounts of Mg and Be in aluminium alloys is described. The samples are dissolved in HCl and examined by the rotating-disc technique, a Hilger medium quartz spectrograph and uncontrolled spark source being used. A description is given of the apparatus, general procedure and preparation of standard solutions. *Procedure*—A 1-g sample is dissolved in 25 ml of HCl (1 + 1), the volume is reduced to between 10 and 15 ml and the cooled soln., made up to 25 ml is returned to the original beaker. Part of the sample is then transferred to a silica combustion boat and placed on the platform of the solution apparatus. The platform is raised until the disc is rotating in the soln. at a depth of $\approx \frac{1}{16}$ in. The same disc may be used for all exposures of the same sample, but the counter-electrode is changed for each exposure. To make the periphery of the disc more porous, a 30-sec. pre-spark is given before the first exposure and a 10-sec. pre-spark before each subsequent exposure. Comparison with available data suggests that the method described is as good as, if not superior to, present chemical methods in reproducibility.

G. C. JONES

658. Use of EDTA (disodium salt) for the rapid determination of calcium and magnesium in limestone and dolomite. M. M. Sochevanova (Inst. Geol. Sci., USSR Acad. Sci.). *Zavod. Lab.*, 1955, **21** (5), 530-532.—The sample (0.5 g) of silicate or carbonate is boiled with dil. HCl , the solution is filtered, treated with NH_4Cl and methyl red indicator, and the hydroxides are pptd. by the addition of aq. NH_3 to the hot solution. After filtration the solution is made up to 250 ml in a calibrated flask. A portion (50 ml) is mixed with 50 ml of water, 10 ml of a buffer solution (20 g of NH_4Cl dissolved in a small amount of water, mixed with 100 ml of 25 per cent. aq. NH_3 , and made up to 1 litre) and titrated with 0.1 N EDTA (disodium salt) in the usual way; the amount used corresponds to the total Ca + Mg. In another portion (100 ml) Ca is pptd. as oxalate and the Mg is titrated with EDTA (disodium salt) in the usual way.

G. S. SMITH

659. Analytical applications of sodium lauryl sulphate. I. The volumetric determination of barium. J. R. Gwilt (1 Newton Ave., London, W.3). *J. Appl. Chem.*, 1955, **5** (9), 471-474.—The method is based on the quant. interaction of Na lauryl sulphate (I) with Ba^{++} to give a ppt. that is insoluble in cold water or alcohol. A known excess of I is added to the soln. of Ba^{++} , the ppt. is filtered off, and unchanged I is titrated with a quaternary ammonium salt, e.g., benzalkonium chloride; methyl yellow, in the presence of chloroform, is used as indicator. **II. Volumetric determination of sulphates.** W. Davey and J. R. Gwilt. *Ibid.*, 1955, **5** (9), 474-476.—The method described above can be used for the determination of SO_4^{--} . The SO_4^{--} in the sample soln. is pptd. as BaSO_4 , excess of Ba^{++} is then pptd. with I, and unchanged I is titrated with benzalkonium chloride.

S.C.I. ABSTR.

660. Analyses of metals by use of ion-exchange resins. I. Determination of cadmium in copper and zinc, and zinc and copper in cadmium. Yukichi Yoshino and Masuo Kojima (Coll. General Educ., Univ. Tokyo, Japan). *Japan Analyst*, 1955, **4** (5), 311-315.—Cadmium adsorbed on a resin column of Amberlite IR-120 is quant. eluted with 160 ml of 0.5 N HCl (1.5 ml per min.) but Cu (< 500 mg) and Zn (< 500 mg) are not eluted. The sample (0.5 g) of Cu (0.001 to 0.3 per cent. of Cd) or Zn (> 0.0003 per cent. of Cd) metal is dissolved in an excess of HNO₃ (1 + 1) and diluted to 100 ml to produce a dil. HNO₃ soln. (< 0.5 N). A suitable portion of this soln. is passed through a column of IR-120 (H), which is then eluted with 0.5 N HCl. The amount of Cd in the eluate, which is free from Cu and Zn, is determined by the dithizone method. This method of separation is also applied to the analysis of micro amounts of Zn (> 0.0002 per cent.) in Cd metal. The sample (1 to 1.6 g) is dissolved in HNO₃ (1 + 1), diluted to 50 ml, passed through the column and then eluted with 0.5 N HCl (160 ml) to remove Cd from the resin. Zinc, which remains on the column, is then eluted with 2 N HCl (80 ml), and determined by the dithizone method. For the analysis of Cu (> 0.00004 per cent.) in Cd, the sample (1 to 15 g) is dissolved in HNO₃ and the excess of HNO₃ is evaporated. The product is dissolved in water (100 to 150 ml) and a small amount of H₂S is added to produce \approx 80 mg of CdS, which is co-precipitated with all the Cu (5 to 30 μ g). The sulphide is centrifuged, dissolved in acid and submitted to fractional elution by a method similar to that for the separation of Zn from Cd. Finally, Cu in the eluate (2 N HCl, 80 ml) is determined by the dithizone method. The use of the anion-exchange resin Dowex 2 for the adsorption of the anionic complex of Cd is less satisfactory, since a small amount of Zn or Cu is also adsorbed. K. SAITO

661. Separation of traces of boron by extraction of tetraphenylarsonium fluoroborate. J. Coursier, J. Huré and R. Platzter (Commissariat à l'Energie Atomique, Saclay, France). *Anal. Chim. Acta*, 1955, **13** (4), 379-386.—Boron is converted into HBF₄, and the tetraphenylarsonium salt of the acid is isolated by extraction with CHCl₃. The equilibria involved in the formation of HBF₄ and the extraction of the salt are considered theoretically, and favourable conditions are determined experimentally. *Procedure*—Polyethylene or platinum apparatus is used. To the solution containing 0.05 to 1 μ g of B add ammonium hydrogen difluoride, or HF and NaF, to produce a concn. of F⁻ < 0.8 M and a pH < 3.2. The vol. should now be 5 ml. Set aside for < 18 hr., add 5 ml of a soln. of 1.046 g of tetraphenylarsonium chloride in 250 ml of CHCl₃, shake for 30 min., and centrifuge. Withdraw the aq. layer with a pipette, add 5 ml of water to the CHCl₃ layer and withdraw it. Extract three times by shaking with 5-ml portions of water. To the CHCl₃ soln. in a platinum capsule add 5 drops of 0.1 N NaOH and 1 drop of phenolphthalein soln. (0.1 per cent. in ethanol) and evaporate to dryness with a surface heater. Treat the residue with 1 ml of N trichloroacetic acid; after 10 min. add 1 ml of turmeric soln. (0.125 per cent. in ethanol) and heat in an oven at 106° \pm 1° C for 60 \pm 3 min. Dissolve the residue in ethanol to produce 25 ml of soln., determine the extinction at 540 m μ and deduce the content of B from a calibration graph. The max. error is \pm 0.04 μ g.

and is independent of the weight of B present up to 0.4 μ g. W. C. JOHNSON

662. Determination of boric acid in nickel-plating electrolytes. I. M. Yurist and P. G. Shakhova. *Zavod. Lab.*, 1955, **21** (5), 539.—An improvement in the method of Freeman and Pritchard (*Plating*, 1953, **40**, 59) is described. A mixture of 2 ml of the electrolyte, 10 ml of water, 10 ml of saturated K₄Fe(CN)₆ solution and 3 drops of bromothymol blue indicator is titrated with 0.1 N NaOH to a greenish-blue tint; 10 ml of glycerol-water (2:1) solution or a mannitol suspension are then added whereby the colour change is reversed, and the solution is again titrated with 0.1 N NaOH to a stable greenish-blue colour. The difference between the two burette readings multiplied by 3.092 gives the boric acid content in grams per litre. A comparison solution is used to assess the end-point in the titrations. G. S. SMITH

663. Titrimetric determination of aluminium in steel. C. Elliott and J. W. Robinson (Post Office Engineering Dept., Birmingham, England). *Anal. Chim. Acta*, 1955, **13** (4), 309-312.—The method of Beck and Szabó (*Brit. Abstr. C*, 1952, 293) is improved by performing both titrations in the same soln., NaF being added before the second titration. *Procedure*—Dissolve 5 g of steel in aq. HCl and oxidise with HNO₃. Evaporate to a paste and make up to 50 ml with conc. HCl. Extract with three 100-ml portions of dichloroethyl ether and discard the extracts. Evaporate the aq. soln. to dryness, dissolve the residue in aq. HCl and dilute to 10 to 20 ml; filter off any SiO₂, wash with dil. HCl and dilute the filtrate to 50 to 100 ml, add 2 to 3 g of NH₄Cl and ppt. the Al⁺⁺⁺ and residual Fe⁺⁺⁺ with dil. aq. NH₃ (1:1) at the boiling point. Boil for 5 min., filter, wash with 1 per cent. aq. NH₃ until free from Mn, Ni, etc., then with 1 per cent. aq. NaCl until free from NH₄⁺. Redissolve the ppt. in dil. HCl, boil off excess of acid, dilute to 20 ml, add 2 drops of indicator (equal parts of 0.2 per cent. soln. of cresol red and thymol blue in water) and make alkaline with 0.2 N NaOH (CO₂-free). If much Fe^{III} is present, dilute the soln. further and add paper pulp to facilitate detection of the end-point. Titrate with 0.1 N HCl to a yellow colour, add neutral 4 per cent. aq. NaF to provide < 5 ml per mg of Al, boil, cool to room temp. and titrate to the same colour as in the first titration. A difference of 1 ml of 0.1 N HCl between the two burette readings = 0.899 mg of Al. The 0.1 N HCl should be standardised against a known amount of Al by the same method. High concn. of F⁻ tend to make the end-point less distinct. W. C. JOHNSON

664. Spectrographic determination, with a carbon arc, of aluminium, iron and titanium in quartz sand. F. Hegemann and C. von Sybel. *Glastech. Ber.*, 1955, **28** (5), 190-194.—The test material (mixed with twice its wt. of carbon powder) is ignited in the cavity (4 mm long, 2 mm diameter) of a carbon electrode of a d.c. continuous arc maintained at 6.5 amp. Intensity-time curves for Al, Fe, Ti, Si, Sn and Ni are presented, the reference elements being Sn for Al, Ni for Fe, and Ni or Si for Ti. The photometric evaluation of the spectrogram for Al₂O₃, Fe₂O₃ and TiO₂ is based on reference curves for artificial test mixtures of known oxide content. A simple visual procedure, in which the standard paper density scale is used, is proposed for the oxides of the remaining trace elements. The

accuracy of the spectrographic method depends on the element, its concn., and the ratio $\text{SiO}_2:\text{C}$. For contents of 0.3 to 0.03 per cent. of Fe_2O_3 , Al_2O_3 and TiO_2 , the accuracy is ± 2.1 to ± 3.5 per cent. for ratios of $\text{SiO}_2:\text{C}$ between 1:2 and 1:4.

D. R. GLASSON

665. Compleximetric titration of indium. K. L. Cheng (Univ. of Connecticut, Storrs, Conn., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1582-1583.—From 0.05 to 0.2 millimole of In can be quickly determined to within 0.5 per cent. by direct titration with 0.01 M EDTA (disodium salt), 1-(2-pyridylazo)-2-naphthol being used as indicator, at pH 2.3 to 2.5 (in the presence of alkali or alkaline-earth metals, Al or Mn^{II}), or pH 7 to 8 (in the presence of Cu, Zn, Cd, Ni, Ag, Hg, etc., and provided that a suitable amount of KCN and ≈ 1 g of K Na tartrate are added). The end-point is a colour change from red to pure yellow; Fe^{III} can be sequestered, at pH 7 to 8, by the addition of KF. The common anions, except those of Bi, Ga, Sn and Pb, do not interfere.

W. J. BAKER

666. Separation and determination of scandium. Spectrophotometric method using alizarin red S. A. R. Eberle and M. W. Lerner (U.S. Atomic Energy Comm., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1551-1554.—Small amounts of Sc can be determined spectrophotometrically to ± 5 per cent. by forming the scandium alizarinsulphonate lake in a soln. buffered with ammonium acetate. Beer's law is valid over the range 10 to 120 μg of Sc_2O_3 per 100 ml. Interfering elements are removed from a soln. of the sample in H_2SO_4 or HCl by the following successive stages: (i) a cupferron- CHCl_3 extraction removes Zr, Hf and other metals, (ii) removal of Th by co-pptn. with Hg as insol. iodate in HNO_3 soln., (iii) extraction of Sc with tributyl phosphate in the presence of HCl (to eliminate Al, Be, U, Cr and rare earths), (iv) remaining traces of impurities are removed by a series of tartrate pptn. with Y as carrier, and (v) a second tributyl phosphate extraction to separate Sc from Y. The Sc in the final organic phase is extracted by shaking the soln. with water, any residual butyl phosphate in the aq. phase being removed by washing with ether. The extinction of the coloured complex is measured at 520 $m\mu$, at a slit width of 0.04 mm, in a 5-cm cell. Extraction data for Sc in HCl-tributyl phosphate systems are listed. The method is applicable to uranium feeds and wastes, and to scandium-bearing ores and minerals (beryl, rutile, etc.).

W. J. BAKER

667. Distinguishing between graphitic and amorphous carbon. P. L. Walker, jun., J. F. Rakaszawski and A. F. Armington (Dept. Fuel Technol., Pennsylvania State Univ., State College, Pa., U.S.A.). *Bull. A.S.T.M.*, 1955, No. 208, 52-54.—The A.S.T.M. "float-and-sink" test and the use of X-ray diffraction patterns for identifying and estimating amorphous and graphitic carbon in admixture are compared. The former test, in which 1:2-dibromoethane is employed as separating liquid, can be used only for mechanical mixtures. For an integral admixture within the same crystallite, e.g., heat-treated carbons or carbon from the decomposition of CO, the X-ray diffraction pattern of the (002) region should be examined and interlayer spacings and peak widths determined. The percentage of graphitic carbon can then be calculated directly. A doublet (002) peak indicates dilution of the graphite with a carbon of inter-

mediate character. The X-ray method can also be used to supplement the "float-and-sink" technique (cf. *Ind. Eng. Chem.*, 1954, **46**, 1651).

W. J. BAKER

668. Errors in determination of carbon dioxide in coal. J. B. Nelson and D. E. Shipley (Brit. Coal Utilisation Res. Assoc., Leatherhead, England). *Fuel, Lond.*, 1955, **34** (4), 404-408.—Chalybite and ankerite may be incompletely attacked, unless finely ground, by aq. H_3PO_4 , owing to coatings of iron phosphates, vitrinite, or fusinite. Coal containing these minerals should therefore be treated with aq. HCl (4 per cent.) to expel CO_2 . Granular $\text{Cu}_3(\text{PO}_4)_2$ is recommended for retaining H_2S .

A. R. PEARSON

669. Contribution to the colorimetric determination of aqueous silicate solutions by means of the molybdate reaction. E. Blasius and A. Czekay (Anorg.-chem. Inst. Techn. Univ., Berlin-Charlottenburg, Germany). *Z. anal. Chem.*, 1955, **147** (1), 1-9.—The influence of the aggregation of silicates when they are colorimetrically determined by the molybdenum blue reaction is studied. The aggregation process depends on conditions such as the silicate concn., the pH value and the foreign electrolyte content, which must be equalised when comparing standard with test solutions.

D. R. GLASSON

670. Recent advances in the analytical chemistry of silicate materials. H. Bennett. *Trans. Brit. Ceram. Soc.*, 1955, **54** (6), 319-332.—A review is given of the rapid and direct methods for the determination of (1) SiO_2 by pptn. of the molybdosilicate with an org. base, e.g., 8-hydroxyquinoline or quinoline (gravimetric 4 hr., volumetric 2 hr., accuracy ± 0.5 per cent.); (2) Al_2O_3 as the oxinate (if the content of SiO_2 is high it must first be removed with HF); (3) CaO and alkali metals with the flame photometer, interference by other ions, and especially by Al_2O_3 , being minimised by using a monochromator instrument, or by sequestering, or by "swamping" with a large addition of Al_2O_3 , or by the addition of SrO, with which the Al_2O_3 interferes in preference to the CaO. The spectrograph has practical application only to qualitative analysis and to the estimation of traces.

J. A. SUGDEN

671. Studies on spectrophotometry. X. Determination of microgram quantities of germanium with quercetin. Yoshinaga Oka and Shigeki Matsuo. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (6), 610-615.—Quercetin (a flavanone) reacts with Ge in neutral soln. (pH 6.4 to 7.1, phosphate buffer) to give a yellowish complex (max. absorption 410 $m\mu$), which is soluble in water containing > 40 per cent. of methanol. The absorption spectrum of quercetin itself has max. at 258 and 375 $m\mu$ and has little influence on the light absorption of the germanium complex at 410 to 440 $m\mu$. The extinctions at 410, 420, 430 and 440 $m\mu$ follow Beer's law for $< 0.5 \mu\text{g}$ of Ge per ml in the presence of an excess of quercetin (> 14 times the equiv. of the Ge) in 40 per cent. methanol. Germanium ($< 120 \mu\text{g}$) is distilled from a 6 to 7 N HCl soln. (at $< 107^\circ\text{C}$) and co-pptd. with $\text{Fe}(\text{OH})_3$ (≈ 40 mg) from the distillate with aq. NH_3 soln. For the removal of Fe, the ppt. is dissolved in N HCl (3 ml) and passed through a column of Amberlite IR-120 (H). A suitable portion of the eluate is treated with phosphate buffer and quercetin soln. and its extinction is measured. No interference results

from the presence of As (< 0.5 mg per ml of the final soln.), Se, Sn and Sb.

K. SAITO

672. Application of paper chromatography to the quantitative determination of germanium. E. Bertorelle and G. Fanfani (Centro di Studi di Chimica Metallurgica del C.N.R., Milan). *Chim. e Ind.*, 1955, **37** (10), 777-779.—Germanium is determined as sulphate solution on paper strips previously "tared" electrophotometrically. Ascending chromatography on strips of Whatman No. 3 paper is performed with 0.15 to 1.5 μ g of Ge as sulphate, with a mixture of acetone, ethyl methyl ketone, HCl and H_2O (85:5:5:5) as eluent. The streak is made transparent and homogeneous by treatment with glycerol-ethanol. The absorption is measured along the strip electrophotometrically by a direct-reading or a recording galvanometer. The curve so obtained is superimposed on the curve obtained in the "tare" of the paper strip. From the area of the peak due to Ge and comparison with standards the amount of Ge can be determined. Under the conditions given, Ge has an R_F value of 0.6.

C. A. FINCH

673. Polarographic determination of tin in ores. D. L. Love and S. C. Sun (Coll. Mineral Ind., Pennsylvania State Univ., Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1557-1559.—The method makes use of the second polarographic wave in a 6 N HCl soln. of Sn^{++} , which corresponds to complete reduction of the chlorostannate complex to metallic Sn at a half-wave potential of -0.52 V vs. the S.C.E. at 25° C. It is applicable to all ores (especially flotation concentrates), alloys, compounds or mixtures containing from 0.01 to ≈ 10 per cent. of Sn. *Procedure*—Fuse quickly ≈ 1 g of sample (≈ 100 mesh) with 8 g of Na_2O_2 in an iron crucible held at bright red-heat for 1 min. Place the cool crucible in a 250-ml beaker containing 150 ml of H_2O , boil to dissolve the melt, remove and wash the crucible, transfer the cool soln. to a calibrated flask (200 ml) and make up to the mark with H_2O . Filter ≈ 50 ml of this soln. into a dry beaker, transfer, by pipette, 25 ml into a calibrated flask (50 ml) and make up to the mark with conc. HCl. (For samples containing > 2 per cent. of Sn add 0.1 ml of 2 per cent. aq. gelatin soln. before adding the acid.) Make a polarogram of the soln. (50 ml) over the range -0.4 to -0.8 V vs. the S.C.E. Convert the wave-height to μA , whence the percentage of Sn can be calculated as $1.075 I_d (\mu A) / \text{sample wt. in g}$. Nickel, W and V should be removed from the soln.; Pb is sequestered by occlusion with the $Fe(OH)_3$ formed during fusion. An analysis takes ≈ 2 hr.

W. J. BAKER

674. Titration of lead with molybdate, with an internal indicator. T. F. Dubrovskaya and N. A. Filippova. *Zavod. Lab.*, 1955, **21** (5), 523-524.—Lead in 50 ml of 2.5 per cent. acetic acid is treated with 10 to 12 drops of 0.3 per cent. diphenylcarbazone in ethanol and titrated with ammonium molybdate until a stable pink colour appears.

G. S. SMITH

675. Determination of lead in steel by use of dithizone. Takayoshi Yoshimori and Shizo Hirano (Nagoya Univ., Chigusa-ku, Nagoya, Japan). *Japan Analyst*, 1954, **3** (6), 470-474.—The separation of a small amount of Pb (< 0.3 per cent.) from a

large amount of Fe is effected by extraction with a soln. of dithizone in CCl_4 from an ammoniacal soln. containing KCN, tartrate and hydroxylamine. The org. layer is treated with HNO_3 to decompose the Pb-dithizone complex and to transfer Pb and a small amount of the Fe present to aq. soln., which is titrated with dithizone- CCl_4 by the extraction titration method. The average deviation from the mean is ± 2 per cent. and the time taken for an estimation is ≈ 30 min. *Procedure*—The sample (0.1 to 0.3 g) is dissolved in 6 N H_2SO_4 (10 ml) and conc. HNO_3 (0.5 ml) and heated until white fumes are evolved. The product is dissolved in water (15 ml), partly neutralised with aq. NH_3 soln. and treated with hydroxylamine hydrochloride (10 per cent., 7 ml), K Na tartrate (40 per cent., 3 ml), dil. aq. NH_3 soln. (until the soln. becomes alkaline) and KCN (20 per cent., 10 to 15 ml). A suitable portion is repeatedly extracted with 5-ml portions of dithizone (6 mg per 100 ml of CCl_4) until all the Pb has been transferred to the org. layers, which are combined and shaken with 1 per cent. HNO_3 (10 ml) to transfer the Pb to the aq. layer. The acid soln. is treated with small amounts of tartrate and hydroxylamine (0.5 ml each), made alkaline with aq. NH_3 soln., treated with KCN (1 ml) and carefully neutralised with 5 per cent. HNO_3 . The product is extracted with small portions of a standard soln. of dithizone in CCl_4 (≈ 4 mg per 100 ml) until no reddish colour is observed in the CCl_4 layer.

K. SAITO

676. Oxidations with alkaline permanganate using univalent thallium for the back-titration. I. Estimation of lead, selenium, tellurium and chromium. I. M. Issa and R. M. Issa (Cairo Univ., Egypt). *Anal. Chim. Acta*, 1955, **13** (4), 323-327.—Previously published methods for the determination of Pb^{II} (*Anal. Abstr.*, 1954, **1**, 1807) and Se^{IV} (*Ibid.*, 1955, **2**, 335), by adding an excess of $KMnO_4$ and titrating the excess with standard formate soln., are improved by the use of a standard soln. of Tl^+ (0.029 to 0.037 N) for the back-titration. Equilibrium is established more rapidly. The method is also applied to the titration of Te^{IV} and Cr^{III} .

W. C. JOHNSON

677. Use of morin in micro-analysis. I. Detection of quadrivalent titanium with morin. G. Almássy (Inst. Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 335-338.—A 0.5 per cent. ethanolic soln. of morin is used as a reagent for detecting Ti^{IV} in the presence of a large excess of other ions, even when these ions yield coloured soln. The Ti-morin complex is reddish-brown, and will detect 0.1 μ g of Ti at a dilution of 1 in 10^7 . Interference from Fe^{III} is eliminated by reduction to Fe^{II} with Zn and HCl, the Ti^{III} also giving a reddish-brown morin complex. Zirconium IV and Th IV also interfere, and they can be removed by the addition of H_3PO_4 . In the presence of Mo^{VI} , W^{VI} , V^{V} , Sn^{II} and Sn^{IV} , a separation of the Ti is made in alkaline soln. after the addition of Fe^{III} . The ppt. is dissolved and the soln. is reduced as described above. The following procedure is given as a spot-test reaction. A drop of test soln. is transferred to a filter-paper, and a drop of distilled water is applied near it to act as a blank. One drop each of N HCl soln. and morin soln. are added to each spot. When the paper is dried, Ti shows up as a yellow-brown spot, whilst the blank is lemon-yellow. The sensitivity is 0.01 μ g of Ti at a dilution of 1 in 5×10^4 .

J. H. WATON

678. Determination of titanium and mixtures of iron and titanium with electrolytically generated ceric ion. R. V. Dilts and N. H. Furman (Princeton Univ., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1596-1599.—With the apparatus described previously (Bricker and Sweetser, *Brit. Abstr. C*, 1953, 463) and the sensitive amperometric end-point procedure, from 50 μ g to 5 mg of Ti can be determined to ± 0.6 per cent. The sample soln. of $\text{Ti}(\text{SO}_4)_2$ is reduced in a Jones reductor, passed into satd. aq. $\text{Ce}_2(\text{SO}_4)_3$ (adjusted to 1.25 V) and titrated coulometrically with electrolytically generated Ce^{IV} in an atm. of N. From 0.013 to 0.16 milli-equiv. of Ti and 0.06 to 0.12 milli-equiv. of Fe can be similarly determined, either when together or separate, with an error of ± 0.7 per cent. The sample soln. is passed through the Jones reductor and drained into a soln. containing < 90 per cent. of the calculated amount of Ce^{IV} required for the titration of Ti. For the titanium end-point, the initial potential (1.3 V) of the generating soln. is lowered to 0.725 V and is then raised to 1.3 V for the Fe^{II} - Ce^{IV} titration. The amounts of Ti and Fe present are calculated from the times required to reach the first end-point and from the first to the second end-point, and the value of the current. In all instances, soln. and impressed-indicator potentials are measured against the lead amalgam - PbSO_4 reference electrode.

W. J. BAKER

679. Volumetric determination of zirconium. An ethylenediaminetetra-acetate method involving back-titration with bismuth. J. S. Fritz and M. Johnson (Iowa State Coll., Ames, Iowa, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1653-1655.—From 13 to 36 mg of Zr in 100 ml of soln. can be determined by adding 10 ml of 0.05 M EDTA (disodium salt), adjusting the pH to 2, adding 1.3 g of thiourea, and then titrating the excess of the disodium salt with 0.05 M $\text{Bi}(\text{NO}_3)_3$ until the yellow colour of the Bi-thiourea complex appears. Few metal cations interfere and the titration can be made in the presence of PO_4^{3-} , SO_4^{2-} , SCN^- , F^- (> 4 mg per 100 ml) and tartrate. Small amounts of Fe^{3+} and Sn^{4+} are titrated quant. with Zr, as is Hf. A slight modification is necessary when moderate amounts of Th, Ti, Nb or Ta are present. The method is as accurate as the amperometric titration procedure of Olson (*Anal. Abstr.*, 1955, **2**, 893).

W. J. BAKER

680. Determination of thorium with β -hydroxy-amino- β -phenylpropionic acid. G. Banerjee (Govt. Coll., Darjeeling, India). *Z. anal. Chem.*, 1955, **147** (5), 348-354.—Thorium can be determined by pptn. with a 1 per cent. soln. of β -hydroxy-amino- β -phenylpropionic acid or its sodium salt, followed by ignition to ThO_2 . The optimum pH ranges for the two reagents are 4.8 to 5.6, and 3.6 to 5.6, respectively. Except for the ions of Hg^{2+} , Fe^{III} and Zr, most metal ions do not interfere. With a double pptn. technique, Th may be separated from cerite earths up to a ThO_2 :cerite-earth-oxide ratio of 1:50 and from U up to a ThO_2 : U_3O_8 ratio of 1:100.

J. H. WATON

681. Potentiometric titration of thorium and cerium nitrates with the glass electrode. K. Pan and T. M. Hseu (Nat. Taiwan Univ., Taiwan, Japan). *Bull. Chem. Soc. Japan*, 1955, **28** (5), 309-312.—Pure aq. $\text{Th}(\text{NO}_3)_3$ soln. in concn. of ≈ 0.001 M can be titrated potentiometrically at 25°C with 0.01 M ammonium or sodium oxalate

by using a glass electrode as the indicator electrode. There are four inflections on the curve: the first (steep) at \approx pH 4.3 corresponds to complete pptn. of $\text{Th}(\text{C}_2\text{O}_4)_2$, whilst the other three, between pH values of 5.4 and 6.3, correspond to the thorium-oxalate complexes. In the same way, a mixture of $\text{Th}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ in dil. aq. soln. can be titrated potentiometrically with aq. NaOH in the presence of 0.5 M NaClO_4 (to repress polymerisation and colloidal adsorption of the hydroxides). The two inflections in the curve, at pH 6.7 and 8.4, correspond to pptn. of $\text{Th}(\text{OH})_4$ and $\text{Ce}(\text{OH})_3$, respectively. The pH value at the coagulation point of $\text{Ce}(\text{OH})_3$ is virtually unaffected by the presence of $\text{Th}(\text{OH})_4$, but the pH value at pptn. of $\text{Th}(\text{OH})_4$ is lowered greatly by the presence of $\text{Ce}(\text{OH})_3$. Whether or not Ce^{IV} and Th^{IV} are determined separately or together by this procedure, correction factors of 1.034 and 1.08, respectively, should be applied to the potentiometric value obtained.

W. J. BAKER

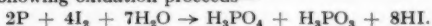
682. Ultra-violet absorption determination of nitrogen dioxide. M. S. Norris, S. A. Fleck and D. H. Lichtenfels (Gulf Res. & Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1565-1568.—A full description is given of the way in which the procedure proposed by Frey and Moore (*Pittsburgh Conf. on Anal. Chem. and Appl. Spectrosc.*, 1953, Paper 54) for the complete determination of nitrogen oxides plus H, CO, CO_2 and N in a mixture has been put on a practical basis. The NO_2 and N_2O_4 are determined by u.v. absorption at 394 m μ , whilst the other oxides of nitrogen are determined by mass spectrometry. The procedure and calculation for the u.v. determination are explained, with emphasis on the chief difficulties. Application of the Verhoek-Daniels equilibrium relations (*Brit. Abstr. A*, 1931, 683) enables all mixtures of NO_2 and N_2O_4 to be analysed provided that the special gas-handling equipment and processes are adopted. The standard deviation (for synthetic mixtures) is $\approx \pm 9$ per cent.

W. J. BAKER

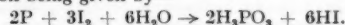
683. Analysis for industry. A. M. G. Macdonald. *Ind. Chem. Mfr.*, 1955, **31**, 515-518.—Colorimetric methods for the determination of nitrates, e.g., in water, sewage, soils and food, are reviewed. (80 references.)

S.C.I. ABSTR.

684. Iodimetric determination of elementary red phosphorus. G. S. Deshmukh and M. Venugopalan. *J. Indian Chem. Soc.*, 1955, **32** (5), 305-308.—A quantitative investigation of the direct oxidation of red P by I dissolved in various solvents is reported. When I is dissolved in aq. KI, the following oxidation proceeds—



If the I is dissolved in an org. solvent (e.g., CCl_4), the first reaction is the pptn. of PI_3 , which is hydrolysed by H_2O added subsequently, the total reaction being given by—

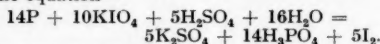


Amounts of 0.005 to 0.05 g of P may be determined by either method with an accuracy of ≈ 1 per cent. In the first method, 0.01 to 0.08 g of red P is swirled with a known vol. of a previously standardised solution of I in KI and with 2 to 3 g of powdered NaHCO_3 , until solution of P is complete (24 to 30 hr.). The residual I is then titrated either with standard aq. $\text{Na}_2\text{S}_2\text{O}_3$ or with As_2O_3 solution in

the presence of NaHCO_3 or a borax-boric acid buffer. In the second method, the red P is shaken for about 30 hr. with 2 to 3 g of NaHCO_3 and 25 to 50 ml of a previously standardised solution of I in CCl_4 . The solution containing pptd. PI_3 is diluted with H_2O , and residual I in the CCl_4 layer is titrated with standard aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution. This reaction has been carried out satisfactorily at room temp. and at 60° to 65° C.

A. JOBLING

685. Volumetric determination of red phosphorus by potassium periodate. G. S. Deshmukh and M. Venugopalan. *J. Indian Chem. Soc.*, 1955, **32** (5), 309-312.—A quant. investigation of the oxidation of red P by aq. KIO_4 in acid solution (0.5 to 2 N H_2SO_4) is reported. The reaction proceeds according to the equation—



Pure dry red P (0.03 to 0.15 g) is weighed into a Kjeldahl flask fitted with a condenser. Ten ml of CCl_4 , an excess of KIO_4 (10 to 12 times the weight of P taken), 2 N H_2SO_4 (20 ml) and H_2O (20 ml) are added and the system is heated under reflux for 4 to 5 hr. When the P has reacted completely, the flask is cooled slowly and the liberated iodine- CCl_4 layer is removed with a blast of hot air. The residual KIO_4 in an aliquot part of the solution is then determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$ solution. In most instances, the error is ± 1 per cent.

A. JOBLING

686. Colorimetric determination of minute amounts of phosphoric, arsenic, silicic and germanic acids by fractional extraction with organic solvents. Toshiyasu Kiba and Mitsuru Ura. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (5), 520-524.—Fractional extraction of molybdate complexes of P, As, Si and Ge was studied with various organic solvents. Molybdophosphate ($< 20 \mu\text{g}$ of P) can be extracted free from As, Si and Ge ($< 500 \mu\text{g}$ each) with a mixture of isobutyl alcohol and chloroform (2:3) ($3 \times 3 \text{ ml}$) from an aq. soln. (10 to 15 ml) of HNO_3 (pH 1.5, $0.14 \pm 0.03 \text{ N}$), containing Na_2MoO_4 (10 per cent.) (1 ml) and NaCl (15 per cent.) (1 ml) (to increase the ionic strength). The extinction of the organic layer is measured with a spectrophotometer at $372 \text{ m}\mu$. The concn. - extinction plot is linear for up to $2 \mu\text{g}$ of P per ml of solvent. For the extraction of the As complex, the acidity of the aq. layer is increased with 10 N HNO_3 (0.85 ml), which is shaken with a mixture of ethyl acetate and *n*-butanol (1:1) (2.5 ml). Chloroform (5 ml) is added to the heterogeneous mixture, which is then shaken for a further 1 min. By this treatment the complexes of Si and Ge are transferred back to the aq. layer and that of As to the organic layer. The organic layer is separated and the aq. layer is extracted in the same way twice more. The organic layers are combined and the extinction, measured at $372 \text{ m}\mu$, is proportional to the concn. of As for up to $2 \mu\text{g}$ per ml. The presence of Si ($< 500 \mu\text{g}$) and Ge ($< 300 \mu\text{g}$) does not interfere with the extraction of As ($< 60 \mu\text{g}$ per ml). The molybdates of both Si and Ge are successively extracted with *n*-butanol from the aq. layer. Attempts at fractional extraction met with little success. The butanol soln. is shaken with 0.04 N NaOH (6 ml) to transfer both molybdates to the aq. layer, which is made up to 10.0 ml with 5 per cent. oxalic acid soln. The extinction is measured at $372 \text{ m}\mu$ to give the sum of Si and Ge. No decomposition of the molybdate complex takes

place at $< 20^\circ \text{C}$. The soln. is then heated in a bath of boiling water for 1 min.; the germanium molybdate complex is completely decomposed, whereas the silicon complex remains unchanged. By measuring the extinction of the product, the amount of Si can be determined and that of Ge calculated.

K. SAITO

687. Cerimetric estimation of phosphite and hypophosphite: silver salt catalysis. K. Bhaskara Rao and G. Gopala Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1955, **147** (4), 274-279; 279-283.—The cerimetric method of Bernhart (*Anal. Abstr.*, 1955, **2**, 903) for estimating phosphite and hypophosphite is found to give irregular results if the soln. is heated on a water bath, even if the heating is continued for as long as 2 hr. In both determinations, quant. results are obtained by heating for 30 min. on an electric hot-plate so that the temp. reaches $\approx 110^\circ \text{C}$. The method, however, is inconvenient, as liquid may be lost by bumping. In the presence of Ag_2SO_4 as a catalyst, the oxidation of phosphite or hypophosphite to phosphate is complete at the temp. of a boiling-water bath. Only a slight excess of $\text{Ce}(\text{SO}_4)_2$ need be used, and the concn. of H_2SO_4 required is much lower.

J. H. WATON

688. Nickel deposition by chemical reduction. A rapid method of estimation of hypophosphite [in plating baths]. A. Goswami (Nat. Chem. Lab. India, Poona). *J. Indian Chem. Soc., Ind. Ed.*, 1955, **18** (2), 116-117.—In an acidic medium, the oxidation of hypophosphite with I proceeds only to phosphite, even at 70°C , and is complete in 20 min.; the normal iodine oxidation method requires 12 to 18 hr. for completion. *Procedure*—Hypophosphite soln. (10 ml), H_2SO_4 (1:5) (10 ml) and 0.1 N I (40 ml) in a flask fitted with a ground-glass stopper are allowed to react for 20 min. after immersion of the flask in a water bath at 70°C . A continuous seal of KI soln. (15 per cent.) is maintained between the mouth of the flask and the stopper to ensure reproducible results. After being cooled, the soln. is back-titrated with 0.1 N thio-sulphate, with starch as indicator. The accuracy is ± 2 per cent. with soln. containing 0.056 to 0.072 g of hypophosphite.

G. HELMS

689. Determination of the pyrophosphate ion in copper-phosphate electrolytic baths. I. G. Lakomkin (Leningrad Tech. Inst.). *Zavod. Lab.*, 1955, **21** (5), 540-541.—The electrolyte (10 ml), which contains copper salts, pyro- and ortho-phosphates, and tartrates, is diluted to 100 ml with water, and 20 ml mixed with $\approx 40 \text{ ml}$ of water are acidified to methyl orange with HCl or H_2SO_4 and passed through a column of SBS Cationite, which has been treated with 6 N HCl and then washed with water. This operation removes copper salts. The filtrate and wash water (200 to 250 ml) is titrated, in the presence of bromophenol blue, with 0.1 N NaOH to a blue colour, 30 ml of 2 per cent. ZnSO_4 solution (neutralised to the same indicator) are added and the titration is continued to the appearance of a stable blue colour. The volume required after the addition of ZnSO_4 is calculated to P_2O_7 .

G. S. SMITH

690. Researches on poly- and meta-phosphates. V. Characterisation reactions of poly- and meta-phosphates by precipitation by various basic organic compounds. J. P. Ebel, J. Colas and N. Busch

(Fac. de Pharm., Strasbourg, Germany). *Bull. Soc. Chim. France*, 1955, (9), 1087-1093.—Solutions (≈ 1 per cent.) of amines in acetic acid (concn. ≥ 10 per cent.) precipitate phosphates (≈ 1 per cent.) selectively and in some instances nearly quantitatively. Under these conditions aniline, *p*-phenylenediamine, *m*-phenylenediamine, *m*-tolenylenediamine, phenylhydrazine and piperazine precipitate only polyphosphates with fairly long chains, 2-naphthylamine all phosphates except trimetaphosphate, benzidine all phosphates, and diaminobenzidine and *o*-tolidine precipitate all except ortho- and trimetaphosphates. Increase in the acidity reduces the number of phosphates pptd. Thus 2-naphthylamine in 30 per cent. acetic acid fails to precipitate ortho- and pyro-phosphates, in 40 per cent. acid triphosphate is soluble, in 60 per cent. acid a vitreous polyphosphate with a $\text{Na}_2\text{O}:\text{P}_2\text{O}_5$ ratio of 8:5 is not pptd., in 80 per cent. acid a vitreous polyphosphate with ratio 3:2 is not pptd., and in conc. acetic acid only Graham's salt and a vitreous polyphosphate of ratio 11:10 are pptd. The quant. pptn. is investigated. Addition of alcohol increases the quant. recovery but destroys the selectivity.

E. J. H. BIRCH

691. Chromatographic examination of metallic ions. II. Stability of antimony halide compounds. E. C. Martin (N.S.W. Univ. of Technol., Broadway, N.S.W., Australia). *Anal. Chim. Acta*, 1955, **13** (4), 353-356.—The R_F values of the antimony halides and Sb tartrate have been determined in butanol saturated with 2 *N* aq. solutions of HF, HCl, HBr, HI and tartaric acid. The covalent salts, SbCl_3 , SbBr_3 and SbI_3 , have high R_F values, while SbF_3 , which is largely ionic, has a much lower value. The tartrate, in evidence of its ionic nature, has an R_F value close to that of SbF_3 . When the fluoride or tartrate is chromatographed in butanol saturated with 2 *N* HCl, HBr or HI, the R_F value rises to the same level as that of the other halides in consequence of the formation of the more stable covalent halides. The partition coefficients of all these compounds for butanol-2 *N* acid are recorded. Some conclusions are also drawn as to the relative stabilities of the covalent halides.

W. C. JOHNSON

692. Amperometric titration of bismuth. A. K. Zhdanov, V. A. Khadeev and G. F. Murtazinova (V. I. Lenin Central Asia State University). *Zavod. Lab.*, 1955, **21** (5), 518-522.—Bismuth in the presence of 8-hydroxyquinoline and sufficient acid to prevent hydrolysis of the bismuth salt and pptn. of bismuth oxinate is titrated amperometrically with a dropping-mercury electrode or a rotating platinum-wire electrode at -0.9 V vs. the S.C.E. (bismuth cathodic current) or at $+0.10$ V and $+0.45$ V, respectively (iodine anodic current), with 0.6 or 0.4 *N* KI. Sulphate and nitrate in large concn. have no effect and chloride does not interfere at concn. ≥ 0.1 *M* if the acidity is sufficiently high. There is no interference by Al, Zn, Co, Ni, Cr and Mn in large amounts. Lead interferes but, in 2.5 *N* HNO_3 with excess of Na_2SO_4 , Bi can be titrated satisfactorily in the presence of the pptd. PbSO_4 ; Cd and Cu must be absent.

G. S. SMITH

693. Colorimetry of bismuth by comparison with potassium chromate. P. Alberto Barreto and B. Ortigui. *Afinidad*, 1955, **32** (149-150), 90.—The method of Condal (*Afinidad*, 1953, **30**, 7), is applied, with a Dubosq colorimeter and a clear

blue filter. Absorption through solutions of KBiI_4 in an excess of KI when plotted vs. concn. of Bi on semi-log paper gives straight-line graphs, as does the absorption of K_2CrO_4 solutions when plotted vs. concn. The concn. of an unknown solution of Bi can therefore be read easily in terms of a K_2CrO_4 solution of equal absorption.

D. LEIGHTON

694. Colorimetric micro-determination of quinquevalent vanadium by an activated reaction. G. Almássy and Z. Nagy (Inst. Med. Chem., Med. Univ., Debrecen, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 339-344.—Vanadium is estimated colorimetrically by the bluish-green dye produced by the oxidation of aniline in strong HCl, in the presence of oxalate ions. The determination can be carried out in the presence of many other metals, including Fe, Al, Ca and Mg. Chloride ions must first be removed by evaporation with conc. HNO_3 . *Procedure*—Not more than 2 ml of soln., containing 10 to 100 μg of V and made 1.0 *N* with respect to HNO_3 , are introduced into a 1-cm cell. The vol. is made up to 2 ml with *N* HNO_3 soln., and 0.5 ml of a H_3PO_4 soln. (1:2) is added to remove the interference from Fe^{III} . Saturated Na oxalate soln. (0.5 ml) is added, followed by 1 ml of a soln. containing 10 ml of aniline dissolved in 40 ml of concn. HCl and 50 ml of H_2O and clarified with animal charcoal. After allowing the soln. to stand for 4.5 min., the extinction of the soln. is measured, an S72 filter being used. A reference soln. is prepared in another 1-cm cell from an equal vol. of test soln. made up to 2 ml with *N* HNO_3 , to which are added 0.5 ml of H_3PO_4 , 0.5 ml of Na oxalate soln. and 1 ml of HCl soln. (1:4).

J. H. WATON

695. Determination of oxygen in sodium and in sodium-potassium alloy by the butyl bromide method. L. Silverman and M. Shideler (North Amer. Aviation, Inc., Downey, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1660-1662.—Modifications of the butyl bromide method for determining O in Na (*Anal. Abstr.*, 1954, **1**, 1244) are described; details of tools for breaking the glass capsule and for cutting the Na are given. The organic reagents can be purified more effectively and rapidly by a chromatographic procedure. Liquid eutectic Na-K alloy can be handled by an initial freezing and then controlling the rate of reaction by the temp. After the K has reacted with ≈ 10 to 15 per cent. v/v of butyl bromide mixture at 35° C, the reaction with Na is hastened by increasing the content of butyl bromide mixture to ≈ 40 per cent. v/v. The exact composition of the alloy must be known.

W. J. BAKER

696. Vacuum-fusion analysis of titanium, zirconium and molybdenum. Determination of oxygen by the iron-bath technique. R. S. McDonald, J. E. Fagel, jun., and E. W. Balis (Gen. Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1632-1636.—A modified vacuum-fusion apparatus and procedure for determining the content of O in a metal, with an iron bath in a graphite crucible, is described. The new method ensures that the sample dissolves completely without the usual solidification (caused by carbon contents of ≥ 12 per cent. in the metal) that occurs after ≈ 1 hr. and leads to low recoveries of O. More accurate results are obtained by an initial out-gassing of the crucible, followed by out-gassing of the iron bath for 1 hr. only, at $\geq 1800^\circ$ C, lowering

the temp. to $\approx 1200^\circ\text{C}$, adding 1 to 2 g of Sn and raising the temp. to 1600°C , before the addition of the sample with from 1 to 3 g of steel (as a flux). The temp. is then raised to 1800°C , and the gas is analysed after a 30-min. collection. By adding more Sn and Fe to the crucible between samples, 4 samples can be analysed in a crucible. The Sn prevents absorption of evolved gases by active surfaces. The results are corrected for the known oxygen content of the added Fe and steel.

W. J. BAKER

697. The estimation of ozone at high dilutions by electrometric and colorimetric methods. J. N. Pring (Davy-Faraday Lab., Royal Institution, London). *J. Appl. Chem.*, 1955, **5** (7), 338-347.—A highly sensitive method, based on the measurement of the oxidation potential of a bromine-hydrobromic acid electrode, is described for the determination of ozone at high dilutions. The procedure, which is determined by an equilibrium condition, does not require complete absorption of the highly dilute ozone by the reagent and is independent of the total volume of air passed. The method is not appreciably affected by oxides of nitrogen or other oxidising bodies at concentrations that occur in the atmosphere. The results are compared with those obtained by the KI-starch-paper method and the limitations of the different techniques are discussed.

O. M. WHITTON

698. Determination of sulphur in synthesis gas. J. Klíma and V. Procházká. *Práce Ust. Vyzh. Využ. Paliv*, 1955, (1-9), 78-100.—The gas is led at 20 to 25 litres per hr. over silica gel, on which the sulphur compounds are absorbed. Desorption is carried out in a combustion furnace in two sections, with simultaneous oxidation with air. The compounds are oxidised further with ammonium hypobromite to sulphates, pptd. with 0.0002 N BaCl_2 and the excess of BaCl_2 is determined polarographically.

FUEL ABSTR.

699. Accurate measurement of hydrogen sulphide in town's gas. J. S. Hart (Evans Electrochemical Ltd., Harlow, England). *Chem. & Ind.*, 1955, (37), 1148-1149.—The density of the stain on lead acetate paper, produced by a known vol. of gas passed through it, is measured by a selenium barrier layer photo-electric cell in a specially designed hydrogen sulphide meter, the construction and operation of which are described in detail.

S.C.I. ABSTR.

700. Oxidimetric methods for the volumetric estimation of sulphite. K. Bhaskara Rao and G. Gopala Rao (Andhra Univ., Waltair, India). *Anal. Chim. Acta*, 1955, **13** (4), 313-322.—Previous authors have found KMnO_4 , $\text{Ce}(\text{SO}_4)_2$ and $\text{K}_2\text{Cr}_2\text{O}_7$ to be unsuitable for the determination of SO_3^{--} because mixtures of SO_4^{--} and $\text{S}_2\text{O}_8^{--}$ are obtained. It is now shown that SO_3^{--} are oxidised quant. to SO_4^{--} when added to an excess of KMnO_4 in N acetic acid if 1 ml of 1 per cent. aq. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is present in 50 ml of the mixture. The excess of KMnO_4 is then titrated with standard $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$. Alternatively, the reaction may be carried out in 0.5 to 4 N H_2SO_4 with the addition of 1 ml of ICI as catalyst (a soln. of 0.279 g of KI and 0.178 g of KIO_3 in 250 ml of water diluted to 500 ml with conc. HCl). The same catalyst serves for the oxidation of SO_3^{--} with $\text{Ce}(\text{SO}_4)_2$ in 7.5 N H_2SO_4 . The excess of $\text{Ce}(\text{SO}_4)_2$ is titrated with standard $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, with the use of ferroin as indicator. No catalyst is necessary with $\text{K}_2\text{Cr}_2\text{O}_7$,

if the reaction proceeds in 0.5 to 1.0 N HCl or in 1 to 3 N acetic acid; at higher concn. of HCl, CuSO_4 or ICI is necessary. With $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.1 to 5 N H_2SO_4 , ICI must be added. Sulphite also reacts quant. with a slight excess of sodium vanadate in 5 N HCl containing 1 ml of ICI soln. After 5 min. at room temp. the excess of vanadate is titrated with standard $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$, N-phenylanthranilic acid being used as indicator.

W. C. JOHNSON

701. Direct potentiometric titration of free sulphur trioxide in oleum with water as titrating agent. H. B. van der Heijde (Koninklijke Shell Lab., Amsterdam, Holland). *Chem. Weekbl.*, 1955, **51** (46), 823-826.—Improvements of the method first reported by Sponar (*Coll. Czech. Chem. Commun.*, 1951, **16**, 526) are given. The potentiometric arrangement, which includes an Hg-Hg $_2$ SO $_4$ reference cell and chloranil electrode, and special provision for cooling, is described in detail. *Procedure*—Weigh accurately 80 to 100 g of the oleum to be tested into a closed titrating vessel, connect to a magnetic stirrer and cooling system, and titrate by adding H_2O dropwise, keeping the temp. first at 0° to 35°C , and then at 11° to 35°C , until the potentiometric end-point is reached. The error is $< \pm 0.2$ per cent. SO_3 for 20 per cent. oleum. Results are consistent and reproducible.

H. A. FISHER

702. Determination of the water content of sulphuric acid containing several per cent. of organic matter. B. Labryère (Lab. of Koninkl. Sulphuric Acid Wks., c/o Ketjen N.V., Amsterdam, Holland). *Chem. Weekbl.*, 1955, **51** (46), 826-827.—The modification of Sponar's method (*cf. Anal. Abstr.*, 1956, **3**, 701) is adapted to the determination of water in H_2SO_4 ; the aq. H_2SO_4 is titrated with 30 per cent. oleum, in the apparatus described, the end-point being indicated by a sudden change of the potential; the temp. is kept at 11°C , to reduce reactivity of organic impurities. The method is claimed to be convenient and accurate, giving reproducible results, and is recommended for routine determinations.

H. A. FISHER

703. A rapid determination of sulphuric acid in acid mixtures by use of aniline. Tetsuro Murakami (Kogakuin Univ., Shinjuku, Tokyo, Japan). *Japan Analyst*, 1954, **3** (6), 497-502.—The low solubility of aniline sulphate in aniline (≈ 0.2 mg of sulphate in 20 ml of aniline) enables a rapid (≈ 30 min.) determination of H_2SO_4 in a mixture with HNO_3 or acetic acid to be effected. The presence of water (< 0.4 g for 20 ml of aniline) does not vitiate the estimation. The sample, containing 10 to 50 mg of H_2SO_4 , is treated with aniline (20 ml) and set aside for 5 min. The colourless ppt. is filtered off on a Gooch crucible and washed with small portions of aniline (total 30 ml). The contents of the crucible are transferred to a beaker, diluted with a sufficient amount of water and titrated with 0.1 N NaOH to phenolphthalein. This method appears to be suitable for the determination of free H_2SO_4 in the mixture with acetic acid, acetic anhydride and Na acetate used for the prep. of cellulose acetate.

K. SAITO

704. Colorimetric determination of chromate with o-aminophenyldithiocarbamic acid. E. Gagliardi and W. Haas (Graz Univ., Austria). *Z. anal. Chem.*, 1955, **147** (5), 321-326.—The orange-yellow colour given by the interaction of o-aminophenyldithiocarbamic acid (I) with small amounts

of CrO_4^{2-} can be used for the quant. estimation of CrO_4^{2-} . Maximum extinction occurs at $480 \text{ m}\mu$, but good results are obtained with a Lange colorimeter and a blue-green filter. The acidity should be ≈ 0.02 to 0.07 N with a mineral acid. A large excess of alkali-metal, ammonium and heavy-metal salts does not interfere, but excess of Fe, Co, V, Ag, Hg and Sb compounds should be avoided. The measurements are made in 100 ml of an aq. soln. containing 0.1 to $1.0 \mu\text{g}$ of Cr per ml, 50 ml of a 0.05 per cent. aq. soln. of the ammonium salt of I and 5 ml of N HCl . Water is used as a blank.

J. H. WATON

705. Methods for the analysis of iron and steel. XXXIV. Molybdenum in iron and steel. (Absorptometric method.) British Standards Institution (2 Park St., London). B.S. 1121: Part 34: 1955, 8 pp.—The sample (0.5 g) is dissolved in HCl (20 ml) and HNO_3 (5 ml), the soln. is evaporated to fuming with a 50 per cent. soln. of H_2SO_4 (10 ml) and cooled. More of the H_2SO_4 soln. (15 ml) is added and the soln. is diluted to 100 ml. Tungsten, if present, is kept in soln. by the addition of citrate, and insoluble material is removed by filtration. An aliquot (20 ml) is taken and the molybdenum thiocyanate colour is developed with a 20 per cent. soln. of ammonium thiocyanate (5 ml), the associated iron colour being reduced with a 10 per cent. soln. of stannous chloride (10 ml) in the presence of a titanous salt, and the mixture is diluted to 50 ml. The colour difference between this and a similar soln. without thiocyanate is measured at 500 to $550 \text{ m}\mu$ and related to a calibration graph. Appreciable amounts of Cu, Co and V interfere, but corrections can be made.

J. O. LAY

706. Determination of impurities in tungsten metal. I. Determination of copper. R. H. A. Crawley (The British Thomson-Houston Co., Rugby, England). *Anal. Chim. Acta*, 1955, **13** (4), 373-375.—The A.S.T.M. ("Methods for Chemical Analysis of Metals") procedure for Cu in tungsten is criticised and the following method is preferred. Dissolve the sample (1 g for contents of Cu up to 0.01 per cent.) in 2 ml of conc. HNO_3 and 2 ml of conc. HF . Add 2 ml of conc. H_3PO_4 and evaporate to a syrup to remove the HNO_3 and HF . Cool the residue, dissolve in 25 ml of 4 per cent. aq. Na citrate, add 1 g of $\text{NH}_4\text{OH}\cdot\text{HCl}$ (to reduce Cu^{2+}), 20 ml of 20 per cent. aq. Na acetate and 10 ml of a 0.1 per cent. ethanolic soln. of neocuproine (2:9-dimethyl-1:10-phenanthroline). Set aside for 10 min., shake with 10 ml of CHCl_3 for 1 min. and separate. Repeat the extraction with 5 ml of CHCl_3 , dilute the extracts to 50 ml with ethanol and measure the extinction in the Spekker absorptiometer, with Ilford spectrum violet filter 601. Prepare a calibration curve with aliquots of standard copper soln. **II. Determination of iron.** R. H. A. Crawley and M. L. Aspinall. *Ibid.*, 1955, **13** (4), 376-378.—Existing methods for the determination of Fe in tungsten are not suitable for iron contents < 0.12 per cent. For such concn. the following procedure is proposed. *Reagents*—(a) A 0.05 per cent. soln. of bathophenanthroline (4:7-diphenyl-1:10-phenanthroline) in ethanol. (b) Ten per cent. aq. sodium dithionite (50 ml) treated with 10 ml of reagent (a) and extracted with two 10-ml portions of CHCl_3 to remove Fe^{2+} . This reagent must be freshly prepared. (c) Ten per cent. aq. citric acid (500 ml) treated with 5 ml of aq. cupferron (2 per cent.) and, after 15 min., extracted with five 20-ml portions of CHCl_3 to remove Fe^{2+}

and excess of cupferron. (d) Ten per cent. aq. NaOH boiled for 10 min. with 1 ml of aq. MgCl_2 (2 per cent.) and filtered to remove Fe^{3+} . *Procedure*—Dissolve 1 g of W in 2 ml of conc. HF and 1 ml of conc. HNO_3 . Add 20 ml of reagent (c) and evaporate to dryness on a water bath. Dissolve the residue in 10 ml of reagent (d) and add 20 ml of reagent (c). The pH should now be between 4 and 7. Add 20 ml of reagent (b) and, after 15 min., 20 ml of reagent (a). Extract the red Fe^{3+} complex with 10 ml of CHCl_3 and then a further 5 ml. Dilute the extracts with ethanol to 50 ml and measure the extinction in a Spekker absorptiometer, with an Ilford spectrum green 604 filter. Prepare a calibration graph with a standard iron soln.

W. C. JOHNSON

707. Volumetric determination of bromide and iodide in a mixture of the three halides: application to silver halides. H. Chateau (Kodak-Pathé, Vincennes, France). *Sci. Industr. Photogr.*, 1955, **26**, 41-46.—The technique of Kolthoff and Yutzy for the determination of Br^- in the presence of Cl^- is modified to permit determination of Br^- and I^- in a mixture of the three halides. The Br^- and I^- are oxidised to bromate and iodate by heating the soln. to boiling with NaClO at pH 5.5 to 5.6, and the excess of NaClO is removed by K formate. The soln. is cooled, the pH adjusted to 4.1 and the IO_3^- are reduced quant. by KI and determined by titration with $\text{Na}_2\text{S}_2\text{O}_3$. To determine Br^- , the iodine arising from the iodate is reduced by the formate present in the soln. by heating. After being cooled, the mixture liberates 6 atoms of I per initial Br^- on addition of 25 ml of 6 N H_2SO_4 to 150 ml of soln. The technique can be used for the micro-determination of Br^- and I^- , and 1 mg of Br or I can be determined in the presence of 200 mg of the other with a precision better than 2 per cent. The technique can be applied to mixtures of silver halides if the halide ion is first liberated by treating the silver salts with hydroxylamine in alkaline soln.

CHEM. ABSTR.

708. Spectrophotometric studies on organometallic complexes used in analytical chemistry. II. The composition and the dissociation constant of the ferrous complex of nitroso-R salt. Yoshinaga Oka and Masatoshi Miyamoto. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (6), 672-675.—The composition and the dissociation constant of the ferrous complex of nitroso-R salt were studied by the measurement of the absorption spectrum and potentiometric titration (glass electrode). It was found that there are three different kinds of complex salt, one having the molar ratio 1:2 (Fe: nitroso-R) and the others 1:3. The last two complexes can be distinguished from each other by their stabilities; the more stable one has the dissociation constant 1.0×10^{-22} (at 25°C) and appears to play an important role in the colorimetric determination of Fe^{2+} with nitroso-R salt.

K. SAITO

709. Alternative to the Zimmermann-Reinhardt reagent in the estimation of iron from ores. K. M. Somasundaram and C. V. Suryanarayana (Annamalai Univ., Annamalaiagar, India). *Z. anorg. Chem.*, 1954, **277**, 181-187.—Sodium acetate and borax have been shown (*Current Sci.*, 1953, **22**, 148) to be good substitutes for the Zimmermann-Reinhardt reagent when pure soln. of Fe are titrated, but to fail when the iron soln. is prepared from res. Mixtures of K_2SO_4 or Na_2SO_4

with KF are effective in these instances. It is recommended that 35 ml of a mixture (6:1) of a 10 per cent. soln. of K_2SO_4 and KF be used, or 25 ml of a mixture (5:1) of a 30 per cent. soln. of Na_2SO_4 and KF, for titrations requiring ≈ 20 ml of ≈ 0.1 N $KMnO_4$. An excess of HCl should be avoided.

J. H. WATON

710. The polarographic determination of iron and copper in high-purity aluminium (99.9 to 99.99 per cent.). R. Neumann (V.E.B. Leichtmetallwerk, Rackwitz, Germany). *Z. anorg. Chem.*, 1955, **279**, 234-240.—The analysis is carried out in HCl solution, and by using a sufficiently high galvanometer sensitivity (e.g., $\frac{1}{2}$) it is possible to determine the height of the $Fe^{3+} \rightarrow Fe^{2+}$ step very accurately. If Zn is also to be determined, it is essential to ensure complete removal of excess of HCl by evaporation.

C. J. KEATTCH

711. Methods for the analysis of iron and steel. XXXV. Aluminium in iron, steel and ferro-alloys (after mercury cathode separation). British Standards Institution (2 Park St., London). B.S. 1121: Part 35: 1955, 8 pp.—Adjust the soln., after mercury cathode analysis (*Anal. Abstr.*, 1956, **3**, 712), to 300 ml and boil with Br (2 ml). Add NH_4Cl (1 g), adjust the temp. to $80^\circ C$ and add aq. NH_3 soln. (50 per cent.), slowly, with shaking, until the soln. is just alkaline. Boil the soln., allow the ppt. to settle, then filter off and wash the ppt. Dissolve the ppt. with hot 50 per cent. HCl, add H_2SO_4 (5 ml) and heat to fuming. Dilute, oxidise with HNO_3 , boil, cool to $10^\circ C$ and add $KMnO_4$ soln. (0.5 per cent.) until the soln. is just pink. Add 5 per cent. cupferron, slowly, with stirring, until pptn. of the complexes is complete. Filter the soln. through a paper-pulp pad, wash the filter with dil. HCl-cupferron soln. and discard the ppt. Add HNO_3 (20 ml) to the filtrate, and heat to fuming; repeat until all organic matter is destroyed, then dilute to 70 ml. Add tartaric acid soln. (20 per cent.) (5 ml) and neutralise to methyl red with aq. NH_3 soln. (50 per cent.). Add KCN soln. (10 per cent.) (10 ml), heat to $60^\circ C$, add saturated ammonium sulphide soln. (25 ml), digest for 10 min. at $60^\circ C$, cool, filter, and wash with dil. ammonium sulphide soln. to a vol. of 150 ml. Boil the filtrate, add 8-hydroxyquinoline soln. (5 per cent.) (8 ml), dropwise, with constant stirring, digest at $90^\circ C$ for 10 min., collect the ppt. on a paper-pulp pad and wash with hot water. Dissolve the ppt. with hot HCl (50 per cent.) (100 ml), wash the pad with hot water, cool and add a measured excess of standard $KBr - KBrO_3$ soln. Shake the soln. and set it aside for 10 min., add KI soln. (20 per cent.) (10 ml) and back-titrate with standard $Na_2S_2O_3$ soln., starch being used as indicator.

J. O. LAY

712. Mercury cathode electrolysis. Recommended method for use in the analysis of iron, steel and ferro-alloys. British Standards Institution (2 Park St., London). B.S. 1121C: 1955, 12 pp.—A prepared sample (10 g) is dissolved in a 10 per cent. soln. of H_2SO_4 (160 ml) and the soln. is filtered into a 600-ml beaker containing 2 kg of Hg (area, 85 sq. cm). The acidity is adjusted by the addition of a 15 per cent. soln. of Na_2CO_3 (50 ml) and the soln. is electrolysed for 2 to 5 hr., a platinum anode of large area being used. The time required for complete electrolysis is dependent on the composition of the sample and is checked by spot tests for Fe and Cr. The soln. is kept below

$40^\circ C$ and the Hg is stirred mechanically or magnetically during the electrolysis. The electrolyte (and washings), siphoned or run off from the beaker, is suitable for the determination of trace elements, e.g., Al, Ti, V and Zr, since all major constituents, i.e., Fe, Cr, Ni, Co, Cu and Mn, are removed. Molybdenum tends to retard electrolysis.

J. O. LAY

713. Steelworks analysis by Quantometer. Anon. *Metallurgia*, 1955, **52**, 101-102.—The application of a direct-reading instrument (Quantometer) for spectrographic analysis to production control in a steelworks is described. By this means 21 elements or compounds in steels, slags, etc., can be determined. The analysis of a melt sample of steel is available in 9 min., which includes transit and preparation time. The accuracy compares favourably with that of wet chemical methods.

S.C.I. ABSTR.

714. Analytical applications of the photochemical action of light. I. Determination of ferric iron by photochemical reduction in the presence of citric and mandelic acids. G. Gopala Rao and G. Aravamudan (Andhra Univ., Waltair, India). *Anal. Chim. Acta*, 1955, **13** (4), 328-333.—The mechanism of the photochemical oxidation of citric acid by Fe^{3+} is discussed. Ferric sulphate (≈ 0.5 mg-equiv.) in 50 ml of citric acid soln. (< 0.02 M) is reduced completely to Fe^{2+} after exposure to sunlight for 30 min., or after 15 min. if mandelic acid is substituted for citric acid. The presence of free H_2SO_4 retards the reduction. After acidifying with H_2SO_4 and H_3PO_4 the Fe^{2+} can be titrated with standard sodium vanadate, diphenylbenzidine or diphenylaminesulphonic acid being used as indicator. After reduction with mandelic acid the Fe^{2+} can be titrated with $Ce(SO_4)_2$ and diphenylamine, diphenylbenzidine or N-phenylanthranilic acid may be used as indicator. W. C. JOHNSON

715. Compleximetric titrations (chelatometry). XII. 1:2-Diaminocyclohexane-NNN'-tetra-acetic acid as a volumetric reagent. Determination of iron, aluminium and titanium. Z. Šir and R. Přibil (Inst. Org. Chem., Prague). *Coll. Czech. Chem. Commun.*, 1955, **20** (4), 871-875.—Aluminium interferes in the indirect compleximetric titration of Fe with 1:2-diaminocyclohexane-NNN'-tetra-acetic acid (Chenta reagent) (I). Aluminium, as well as Ti, forms a stable complex with I in a soln. buffered with pyridine or with a mixture of pyridine, aq. NH_3 and NH_4Cl . All three metals can be determined singly in weakly alkaline pyridine soln. by the addition of an excess of 0.05 M I, the unchanged I being back-titrated with 0.05 N $ZnCl_2$ or $ZnSO_4$ soln.; Eriochrome black T is used as the indicator. When the ions of all three metals are present, Fe^{III} can be determined if Al^{III} and Ti^{III} are complexed by the addition of a 2 per cent. soln. of NH_4F .

J. H. WATON

716. Gas determination in iron and steel [by the vacuum-fusion method]. M. Signora and F. Baldi (Centro Ricerche e Controlli delle Acciaierie e Ferriere Lombarde Falck, Milan). *Chim. e Ind.*, 1955, **37** (10), 794-801.—An improved apparatus is described and illustrated in detail. Results with some types of steel and iron ingots are reported, and conclusions on the gas content in relation to the working process are made. In the determination in iron an anomaly is explained by the presence of methane in the gas extracted. C. A. FINCH

717. Hydrogen in cast iron. B. B. Bach, J. V. Dawson and L. W. L. Smith (B.C.I.R.A., Birmingham, England). *J. Res. Brit. Cast Iron Ass.*, 1954, **5** (9), 490-501.—By heating various types of white cast iron at temperatures between 20° C and 1150° C it has been shown that a temperature between 650° C and 750° C or above 1000° C is likely to cause complete evolution of hydrogen in two hours, but that intermediate temperatures are unsuitable. Temperatures above 1000° C are required for grey cast iron, although the error is small at lower temperatures. Extremely rapid cooling of the sample is required to enable an accurate determination of hydrogen in liquid metal to be made. J. O. LAY

718. Chemical analysis for nitrogen as an indication of the nitride-forming elements in cast iron. L. W. L. Smith (B.C.I.R.A., Birmingham, England). *J. Res. Brit. Cast Iron Ass.*, 1954, **5** (9), 481-489.—Accepting as "HCl-soluble" the nitrogen separated by attack with HCl and as "HCl-insoluble" (derived from nitrides stable to HCl) the additional amount determined after fuming of the residue with H_2SO_4 , it has been shown that titanium and aluminium in cast iron increase the ratio of HCl-insoluble to HCl-soluble nitrogen. Boron does not behave similarly and it is suggested that, although control over the effect of nitrogen on the properties of cast iron by additions of the first two elements is related to the formation of stable nitrides, with boron this control is achieved directly by some other compensating effect. J. O. LAY

719. Determination of iron pentacarbonyl in commercial carbon monoxide. J. Sendroy, jun., H. A. Collision and H. J. Mark (Naval Med. Res. Inst., Bethesda, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1641-1645.—The apparatus and procedure are described, with the precautions to be taken. The gas sample (1 to 2 litres or more) is passed through a train in which the $Fe(CO)_5$ is either condensed in a trap of solid CO_2 (for concn. < 2 mg per litre) or absorbed in pure methanol (for higher concn.). After the system has been flushed with N, the concn. of $Fe(CO)_5$ is determined spectrophotometrically at 235 $m\mu$ in a methanol soln., which should contain from 0.2 to 5 mg of $Fe(CO)_5$ per 100 ml. The error is ± 1.3 per cent. on samples containing < 0.04 mg. Concn. of $Fe(CO)_5$ in commercial CO in steel cylinders are from 0.16 to 18 mg per litre. W. J. BAKER

720. Separation of double carbides of iron and tungsten from chromium carbides. N. M. Popova and K. P. Sorokina. *Zavod. Lab.*, 1955, **21** (5), 527-530.—Selective dissolution of chromium carbides occurs in dil. HCl, preferably in an ethanol medium, e.g., for 3 to 5 mg of the dry carbides in 50 ml of ethanol with 1 or 10 ml of conc. HCl. G. S. SMITH

721. Analysis of iron-pickle liquor by means of ion exchange. S. Fisher and R. Kunin (Rohm and Haas Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1649-1650.—The iron (up to 30 g per litre) and acid (1 to 2 M) contents of pickle liquors can be determined rapidly by exchanging Fe^{++} for H^+ with a sulphonic acid cation-exchange resin, e.g., the hydrogen form of Amberlite IR-120, and then determining the total acidity. A volumetric determination of Fe^{II} is then made on a separate aliquot of the original soln. The initial acidity is the total acidity minus the H^+ equiv. of

the Fe. Results are accurate to ≈ 1 pt. per 1000. W. J. BAKER

722. Redox determination of tervalent and total cobalt in presence of excess tungstate. L. C. W. Baker and T. P. McCutcheon (Univ. Pennsylvania, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1625-1626.—Either total Co or Co^{III} can be determined in the presence of excess of WO_4^{--} , MoO_4^{--} or Fe by a modification of Sarver's rapid volumetric method (*Brit. Abstr. A*, 1933, 924) with ferrous salt and $K_2Cr_2O_7$. A diphenylamine-sulphonate indicator can be used when the ratio of W to Co is < 12.5 (by wt.), but for higher ratios a sharp end-point is attainable only with platinum electrodes and a polarising voltage. In the procedure described, the uncomplexed tungstate is re-oxidised by the addition of 6 N H_2SO_4 and 25 per cent. H_3PO_4 , after the addition of the excess of 0.1 N ferrous soln. and pptn. of $Co(OH)_2$. Excess of 0.1 N $K_2Cr_2O_7$ soln. is then added to the clear pink soln. and the mixture is back-titrated with 0.1 N ferrous soln. to the potentiometric end-point. The procedure for Co^{III} is identical, except that no additions of sodium perborate are necessary (cf. Sarver). W. J. BAKER

723. Paper chromatography of inorganic ions. XI. The behaviour of some cobalt (III) complexes. M. Lederer (Inst. Radium, Paris, France). *Anal. Chim. Acta*, 1955, **13** (4), 350-352.—The R_F values of six Co^{III} co-ordination complexes have been determined in butanol saturated with N HCl, butanol saturated with 1.5 N aq. NH_3 , mixtures of butanol with dil. acetic acid and ethanol, a mixture of acetone and dil. HCl, and water. In organic solvents the least ionised complex travels fastest unless decomposed. In water the complexes with the greater number of ionic charges travel faster than the univalent or neutral complexes. W. C. JOHNSON

724. Direct spectrophotometric determination on paper of chromatographic spots of cobalt and copper. A. Lacourt and P. Heyndryckx (Fac. Sci., Univ. Libre de Bruxelles, Belgium). *Nature*, 1955, **176**, 880-881; *Compt. Rend.*, 1955, **241** (1), 54-56.—A strip of paper bearing the spot or the vaporised reagent is slipped between the wall of the usual spectrophotometric cell and a prismatic, calibrated, glass adapter, with a few drops of water to eliminate air bubbles. Extinctions of vaporised strips with 1-nitroso-2-naphthol or rubeanic acid are reproducible by this method so that the zero of the apparatus can be set on these strips. The extinction of the strip is then measured directly from this zero at 660 $m\mu$ for Cu and 850 $m\mu$ for Co; blanks need be measured only for control. Reference diagrams have been drawn from 0.1 to 3 μg of Co and Cu. Concentrations can be checked within these limits with a reproducibility better than 0.5 per cent. O. M. WHITTON

725. A new colorimetric determination of a small amount of cobalt in nickel metal and its alloys with m-methoxy-o-nitrosophenol. Tetsuya Torii. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (6), 680-684.—The application of the colorimetric determination of Co with m-methoxy-o-nitrosophenol (I) (*Anal. Abstr.*, 1956, **3**, 118) to the analysis of nickel metal and alloys that contain a significant amount of Fe and Cu was studied. The extraction of the cobalt complex with CCl_4 is not affected by the presence of a large amount

of Ni. Interference from Fe (< 5000 times the weight of the Co) can be masked by the addition of ammonium citrate; Cu (< 500 times) is similarly masked by the addition of thiourea (10 per cent.) (10 ml per 1 mg of Cu). This method is recommended for the analysis of 0.01 to 1 per cent. of Co in Ni. *Procedure*—The sample (1 g) is dissolved in HNO_3 (1 + 1) (30 ml) and heated with H_2SO_4 (1 + 1) (20 ml) until white fumes are evolved. The product is dissolved in water (250 ml), filtered, neutralised with aq. NH_3 soln. and made up to 1 litre. A 5-ml portion is treated with ammonium citrate (40 per cent., pH 8.5) (1 ml) and a saturated aq. soln. of **I** (5 ml), and the pH is adjusted to between 7.0 and 8.5 with aq. NH_3 soln. When Cu (> 10 times the weight of the Co) is present, thiourea (10 per cent.) (10 ml) and ammonium citrate (5 ml) are added. After 15 min. the aq. soln. is extracted with CCl_4 (5-ml portions) until a colourless aq. layer is obtained. The org. layers are combined, shaken with Na_2CO_3 soln. (10 per cent.) (10 ml) to remove the excess of **I** and made up to 25 ml. The extinction is measured at 400 m μ . For samples that contain more Fe (e.g., ferronichrom) or Cu (e.g., German silver) the amounts of the masking agents should be increased. The addition of a small amount of H_2O_2 is also advantageous for the masking of a large amount of Fe.

K. SAITO

726. Compleximetric titration of nickel in the presence of cobalt and several other metals. H. Flaschka and R. Puschel (Inst. Inorg. Tech. Anal. Chem., Tech. Hochschule, Graz, Austria). *Z. anal. Chem.*, 1955, **147** (5), 354-360.—The nickel complex with EDTA (disodium salt) is stable in ice-cold soln. at a pH of 2, whilst the complexes of many other metals under these conditions exchange with Bi. *Procedure*—A known excess of EDTA (disodium salt) is added to the soln. to be analysed, sufficient to complex all the metals present except Mn, Ca, Mg, Sr, Ba and univalent metals. Ice is added to keep the temp. at 0° C, and 2 to 3 drops of a 0.1 per cent. soln. of catechol violet are introduced. Standard $\text{Bi}(\text{NO}_3)_3$ soln. is added till the indicator turns to violet or deep blue, and then standard EDTA (disodium salt) soln. is run in until the colour changes to pure yellow. Iron, In, Ga, Bi, Th, Al and Sb, and tartaric, citric, oxalic and hydrofluoric acids interfere. In an alternative procedure, all the metals, including Ni, are titrated with EDTA (disodium salt) in an ammoniacal soln., with murexide as indicator. After the destruction of the murexide with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, all the complexes except that of Ni are back-titrated with $\text{Bi}(\text{NO}_3)_3$, with catechol violet indicator, in ice-cold acid soln.

J. H. WATON

727. Photo-electric colorimetry of platinum with the aid of its phenylthiosemicarbazide derivative: an extraction method. Sumio Komatsu and Kazuyoshi Onishi. *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1955, **76** (6), 661-664.—The platinum complex of phenylthiosemicarbazide (**I**), which is used for the gravimetric analysis of Pt, is soluble in org. solvents. Its soln. in ethyl acetate follows Beer's law for up to 19 μg of Pt per ml (at 710 m μ). **I** itself is also extracted with org. solvents, but its extinction is negligible compared with that of the platinum complex. The sample soln. is made acid with acetic acid to produce a 2 N soln., then treated with **I** (0.01 per cent. in 2 N acetic acid) (2 ml) and set aside for > 3 hr. The soln. (together with the ppt. of the Pt - **I** complex) is shaken with

ethyl acetate (10 ml) for 2 min., and the extinction of the deep-green soln. is measured at 710 m μ . When Hg^{++} or Ag is present, NH_4Cl is added in excess before the addition of **I**. Iron can be pptd. with sodium phosphate, and Au is removed by heating with NaClO_2 , which does not interfere with the interaction of Pt with **I**. In the presence of Pd or Cu, the ppt. of the platinum complex is filtered off and extracted with ethyl acetate as described above; both copper and palladium complexes of **I** are soluble in water and can thus be separated satisfactorily from Pt.

K. SAITO

728. Bomb method for the determination of sulphur and chlorine in coal. Z. K. A. Moszynski (British Coke Research Association, 74 Grosvenor St., London). *J. Appl. Chem.*, 1955, **5** (9), 467-470.—In an improved bomb-combustion procedure, 1.0 g of coal, 0.5 g of Eschka mixture and 5 ml of 10 per cent. aq. ammonium carbonate are ignited in a 250 to 350-ml bomb in O at 25 atm. pressure. After ignition, the bomb is set aside for 10 min., then washed out by normal procedures. The SO_4^{--} are determined gravimetrically with 10 ml of 10 per cent. aq. BaCl_2 and Cl^- by the modified Volhard procedure used in the B.C.R.A. rapid method.

* S.C.I. ABSTR.

729. Simultaneous determination of sulphur and chlorine in coal. L. J. Edcombe (Fuel Res. Stn., London, England). *Fuel, Lond.*, 1955, **34** (4), 429-432.—The sample is burned with Eschka mixture (B.S. 1016/1942). The residue, containing the S and Cl as soluble salts, is extracted with hot water; metal ions in the filtrate are replaced by H by a 30-min. contact with 30 g of freshly regenerated ion-exchange resin (0.2 to 0.4-mm size), followed by passage through a column of the pre-washed resin. Details of the apparatus are illustrated. The eluate is boiled to expel CO_2 and its total acidity and chloride-ion contents are titrated. Comparative tests with the B.S. gravimetric method on 20 coals show average differences of 0.03 per cent. of S and 0.02 per cent. of Cl.

A. R. PEARSON

730. Polarographic methods for analysis of coal ash. F. M. Kessler and L. Dočkalova. *Práce Úst. Vyzk. Využ. Paliv*, 1955, (1-9), 117-139.—Methods for alkalis, Ti, Fe and Ca were examined with a view to saving time. The Abresch method for separating alkalis requires the removal of all other compounds from the soln. and was rejected. The polarographic determination of Ti in the presence of iron was successfully accomplished by decomposition with HF and HClO_4 , and transference to $\text{N H}_2\text{SO}_4$ containing 8 per cent. of urea and satd. with Na oxalate. The determination of Al in the presence of Fe proved impossible. The determination of Fe proved possible in a strongly alkaline soln. containing tartaric acid. Iron, up to 10 per cent. of Fe_2O_3 in the ash, can thus be quickly determined directly in a soln. of the ash after decomposition with HF and HClO_4 . Iron can also be determined in active carbon within ± 3 per cent. Determination of Ca presents difficulties.

FUEL ABSTR.

731. The decomposition of blast-furnace raw materials and slags, steelmaking slags and refractories for the purpose of chemical analysis. [I, II.] E. W. Harpham (Richard Thomas and Baldwins Ltd., Ebbw Vale, Mon., England). *Metallurgia*, 1955, **52**, 45-53; 93-101.—A survey is given of the

methods of decomposition used for the conversion of certain oxide-bearing materials into solutions suitable for the chemical determination of one or more constituents. The materials concerned are: (1) iron- and steel-making raw materials (excluding coke); (2) iron- and steel-making slags; and (3) acid (or siliceous), basic, and neutral refractories. Three categories of decomposition methods are considered. (a) Wet methods which usually depend on attack by aqueous solutions of the mineral acids, used either alone or in combination. A general procedure for acid decomposition at elevated temp. by operating in sealed glass tubes is outlined. (b) Use of fluxes at elevated temp., the fluxes used being generally compounds of the alkali metals, and include hydroxides, peroxides, carbonates, borates, acid sulphates, pyrosulphates and acid fluorides. Directions are given for decomposition by fusion with sodamide; this method is applicable to a large variety of silicate materials. (c) Special decomposition procedures used for the determination of ferrous iron and of the alkali metals in iron- and steel-making materials. The application of these methods is described for iron ores, sinters, tap cinder, etc., manganese ore, limestone, fluorspar, iron- and steel-making slags and refractories. Methods of decomposition with HCl, Na_2CO_3 (fusion), Na_2O_2 (fusion), KHSO_4 (fusion), H_2SO_4 , HClO_4 , $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{B}_4\text{O}_7$ (sinter), $\text{MgO} + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$ (sinter), and $\text{Na}_2\text{B}_4\text{O}_7$ (fusion) are described in detail. (144 references.) S.C.I. ABSTR.

732. New method for the rapid analysis of silicates, rocks, ores, slags, refractories, etc. I. General.

I. Sajó (Res. Inst. Iron Ind., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 233-241.—Many minerals and slags, etc., can be decomposed rapidly by fusion with KOH in a silver dish, after moistening the sample with a few ml of alcoholic KOH. A clear soln. is generally obtained after leaching out in water and acidifying. Should any residue remain, it is filtered off and the filter is re-treated as above without first being ashed. If Na_2O_2 is added during the fusion, other material, including the carbides of Si, W, Co and Ti, as well as Fe-Si, Fe-Cr, calcium silicide and Fe-B, and slags containing Cr_2O_3 can be dissolved. Material with a high iron oxide content is given a preliminary reduction with H or NH_3 in a quartz tube-furnace, or is wrapped in a moist filter-paper, when the carbon content of the paper carries out the reduction during the fusion with KOH. II. Rapid determination of silica. I. Sajó. *Ibid.*, 1955, **6** (3-4), 243-250.—Silica is estimated by pptn. as K_2SiF_6 and titrating the HF formed when the ppt. is hydrolysed by hot water. Procedure—Sufficient sample to contain ≈ 0.05 to 0.1 g of SiO_2 is fused with KOH and the melt is leached out as described above. The vol. of soln. should be kept between 50 and 60 ml. The soln. is acidified with HCl (sp. gr. 1.12) and 10 ml of HCl (sp. gr. 1.19) are added in excess, followed by 10 ml of HNO_3 (sp. gr. 1.4). If there is a high content of SiO_2 , or if a stock soln. is to be made, the melt is leached out with water, and acidified only after considerable dilution. After making up to a suitable vol., a 50 to 100-ml aliquot is used. The acidified soln. is boiled for 1 to 2 min., cooled to between 30° and 40° C and transferred to a plastic beaker with the minimum of water. Whilst the soln. is agitated with a magnetic stirrer, ≈ 1 g of NaF is added, and the soln. is saturated with KCl to give an excess of ≈ 2 to 3 g. After being stirred for 2 to 3 min.,

the ppt. of K_2SiF_6 is separated in a porcelain funnel, under suction, and is washed free from acid with 50 per cent. aq. ethanol saturated with KCl and adjusted with HCl and NaOH until orange to methyl red. The filter is transferred to a 1-litre Erlenmeyer flask, which contains 400 to 500 ml of hot water made alkaline to phenolphthalein. After the flask has been shaken, the HF is titrated with $N/15$ NaOH (for a 1-g sample of ore, rock or silicate) or with $N/35$ NaOH (for a 2-g sample of steel or metal). A blank must be performed on the reagents. If Al and Ti are present, 5 ml of a 20 per cent. CaCl_2 soln. are added before the NaF; the stirring time must be reduced if these metals are present in large amounts. There is no significant difference between these results for the determination of SiO_2 and those obtained gravimetrically. The volumetric results often show more reliability and reproducibility, and are obtained much more quickly. III. Rapid determination of aluminium by a compleximetric method. I. Sajó. *Ibid.*, 1955, **6** (3-4), 251-262.—Aluminium can be determined compleximetrically in weakly acid soln. Excess of EDTA (disodium salt) is back-titrated with a standard soln. of a zinc salt, Eriochrome cyanine R, Na_2HPO_4 , ferro-ferricyanide - benzidine or ferro-ferricyanide - dimethylnaphthidine being used as indicator. The following procedure is recommended for a direct volumetric estimation. An excess of EDTA (disodium salt) is added to an aliquot of the acid stock soln. prepared as described above, which is then warmed to between 30° and 40° C and made just acid to phenolphthalein with aq. NH_3 and HCl (sp. gr. 1.12). The pH is adjusted to between 5 and 6 with the aid of 20 ml of an acetate buffer, the soln. is boiled for 3 min. and then cooled. A soln. (1 ml) of benzidine in glacial acetic acid is added, followed by 1 ml of a ferro-ferricyanide soln. containing 20 ml of 10 per cent. $\text{K}_3\text{Fe}(\text{CN})_6$ soln. and 5 ml of 1 per cent. $\text{K}_3\text{Fe}(\text{CN})_6$ soln. diluted to 100 ml. The excess of EDTA (disodium salt) is titrated with zinc acetate soln. until the indicator turns blue. Then 30 ml of a neutral saturated soln. of NaF are added and the soln. is brought to boiling point. After being allowed to stand 2 to 3 min., the soln. is cooled and a further 1 ml of each of the indicator soln. is added. The EDTA (disodium salt) liberated is then titrated with the zinc acetate soln., the titre being equiv. to the amount of Al present. Titanium interferes and must be removed with a phosphate buffer before the titration, whilst Co should be oxidised with H_2O_2 . Magnesium, Ca, Sr, Ba and Fe do not interfere, nor do Cr, Cu and Mn unless present in amounts > 10 mg. Fluoride ions must be removed before the estimation. If SO_4^{2-} are present or if ZnSO_4 soln. replaces the zinc acetate soln., dimethylnaphthidine must be substituted for benzidine. Two to three drops of a soln. containing 0.3 g in 100 ml of glacial acetic acid are used.

J. H. WATON

See also Abstracts 752, 862, 864, 871, 875, 893, 896.

3.—ORGANIC ANALYSIS

733. Use of silver permanganate in analysis. I. Properties of silver permanganate and of its thermal decomposition product. J. Körbl (Pharm. and Biochem. Research Inst., Prague). *Coll. Czech. Chem. Commun.*, 1955, **20** (4), 948-951.—Solid AgMnO_4 oxidises organic matter violently on heating. Water and CO_2 are evolved quant., whilst

halogen present in the sample remains as silver halide, and S as Ag_2SO_4 and MnSO_4 . Organic N, as well as N from ammonium salts, KCN and other inorganic compounds of N, is oxidised to nitrogen oxides, which partly remain as AgNO_3 with a trace of $\text{Mn}(\text{NO}_3)_2$. The thermal decomposition product of AgMnO_4 reacts similarly but less violently; in addition, it will catalyse the oxidation of CO in air and of NH_3 in oxygen. The thermal decomposition product also shows absorptive powers. Sulphur dioxide is absorbed as Ag_2SO_4 and MnSO_4 , whilst NO_2 can be selectively absorbed from a mixture of CO_2 , O and NO_2 at room temp. as AgNO_3 , particularly if the material is moistened with water. **II. Estimation of carbon and hydrogen in organic compounds.** J. Körbl. *Ibid.*, 1955, **20** (4), 953-961.—The Pregl apparatus for the semi-micro determination of C and H in organic compounds is adapted to the use of the thermal decomposition product of AgMnO_4 as a catalyst. A relatively low temp. of $\approx 450^\circ\text{C}$ is possible, and the whole analysis can be completed in an hour. Halogens and SO_2 are retained by the catalyst, and NO_2 is removed in a tube containing moist catalyst inserted between the H_2O - and CO_2 -absorption vessels.

J. H. WATON

734. Analysis for industry [micro-analytical determination of carbon, hydrogen, oxygen and nitrogen]. J. E. Fildes. *Ind. Chem. Mfr.*, 1955, **31**, 355-356.—New and modified methods for the micro-determination of C, H, O and N in org. compounds are reviewed. (43 references.)

S.C.I. ABSTR.

735. A new method for the determination of oxygen [and carbon] in organic compounds. T. S. Lee and R. Meyer (Univ. Chicago, U.S.A.). *Anal. Chim. Acta*, 1955, **13** (4), 340-349.—Oxygen in compounds of C, H and O is determined by heating the sample with an excess of SrO and graphite in a nickel bomb or a sealed Vycor glass tube. After 3 hr. at 650°C the oxygen in the sample is converted into carbonate. The carbonate is then determined volumetrically. The method was applied to quinol, tartaric acid, benzoic acid and glucose and a max. error of ± 0.3 per cent. of the substance was obtained. Most elements other than C, H and O interfere. Phenol and xanthone are resistant to pyrolysis and yield low results. The procedure is devised from thermodynamic considerations, which are discussed extensively. Carbon in organic compounds can be determined by heating the sample with $\text{Ba}(\text{NO}_3)_2$ and determining carbonate in the ignition product.

W. C. JOHNSON

736. Determination of halogen in organic compounds. Potentiometric micro-titration with silver-amalgamated-silver electrode system. E. C. Cogbill and J. J. Kirkland (Univ. Virginia, Charlottesville, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1611-1613.—The potentiometric titration of halide with AgNO_3 in which the silver-amalgamated-silver electrode system of Clark (*J. Chem. Soc.*, 1926, 749) is used has been adapted to the micro-determination of Cl, Br and I in organic compounds. Ionisable halogen is determined directly in ethanolic soln.; non-ionic halogen is decomposed by the catalytic dry-combustion method before titration. Application to the determination of halogen in organic substances gave a precision of 3 parts per 1000 with 1 to 4 mg of sample.

G. P. COOK

737. Detection and estimation of sulphur in organic material. L. Rosenthaler (Seftigenstrasse

40, Berne). *Pharm. Acta Helv.*, 1955, **30** (7), 282-283.—To an aqueous alkaline solution or suspension of the compound under test add an aqueous sulphate-free solution of NaOCl (12 per cent.) and set aside for 12 hours. Acidify with HCl , filter off any ppt. that does not dissolve even by boiling and add BaCl_2 solution. Quantitative yields of BaSO_4 were given by KSCN , CS_2 , sodium xanthate, allyl or phenyl isothiocyanate, allylthiourea, thiourea, propylthiouracil and methylene blue. Cystine, methionine, ethionine, saccharin and vitamin B_1 gave only small quantities of ppt.; toluene-*p*-sulphonamide gave no ppt., whilst sulphanilic acid and sulphanilamide gave coloured precipitates.

P. S. STROSS

738. Rapid micro-methods for the determination of elements. Simultaneous quantitative micro-determination of phosphorus, sulphur, carbon and hydrogen in compounds containing C, H, O, N, S and P. M. O. Korshun and Ev. A. Terent'eva. *Dokl. Akad. Nauk SSSR*, 1955, **100** (4), 707-709.—The methods, based on the pyrolysis of the organic compound followed by combustion with a large excess of H, previously developed for the determination of P (*cf. Anal. Abstr.*, 1955, **2**, 933) and for the simultaneous determination of C, H and S (*Brit. Abstr. C*, 1952, 520), are combined. The P_2O_5 formed in the combustion is absorbed by powdered quartz, which has been etched with caustic alkali. The time required for a single analysis is about $2\frac{1}{2}$ hr., and the results are accurate to 0.3 per cent. The method is especially suited to compounds with C-P linkages.

F. W. KIRKBRIDE

739. Spectrophotometric determination of methoxyl. A. P. Mathers and M. J. Pro (Internal Revenue Service, Washington, D.C., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1662-1664.—The methoxyl group is converted by hydrolysis into methanol, which is oxidised to formaldehyde with KMnO_4 . The formaldehyde is determined spectrophotometrically after condensation with chromotropic acid. The method is specific for the methoxyl group and was successfully applied to 20 compounds. A modification for micro-determinations is also described.

G. P. COOK

740. Oxidation of hydrazines. I. Volumetric determination of carbonyl compounds with 2:4-dinitrophenylhydrazine. D. J. Barke and E. R. Cole (Univ. Technology, Sydney, N.S.W., Australia). *J. Appl. Chem.*, 1955, **5** (9), 477-482.—The principle of the method is pptn. of carbonyl compounds with a measured excess of 2:4-dinitrophenylhydrazine (I) to form the corresponding hydrazones, which are filtered off, the excess of I being then found by titration with standard KIO_3 . As against this "direct" procedure, a "reverse" procedure is also proposed, in which, after filtration, a measured excess of KIO_3 is added and the mixture titrated with standard iodine solution. The reagents used are: ≈ 2.5 g of I per litre in 2 N HCl , 0.025 M aq. KIO_3 and 0.1 N I in KI solution.

S.C.I. ABSTR.

741. Anomalies in the determination of primary amino groups with nitrous acid. G. Kainz and F. Schöller (Chem. Lab. Univ., Vienna). *Naturwissenschaften*, 1955, **42** (8), 209.—Anomalous behaviour could be detected in at least seven main groups of substances: (i) isonitroso derivatives, (ii) compounds possessing an active methylene group, (iii)

halogenated acetic acids, (iv) phenols with a free *p*- or *o*-position or nitrosophenols, (v) oxidisable sulphur compounds, (vi) five-membered heterocyclic substances, e.g., uric acid, hydantoin, (vii) indole and oxindole derivatives, except those substituted in the α - and β -positions or on the imino nitrogen. The anomalies are much more marked when concentrated nitrite solution (a 500-fold excess) is used than when dilute nitrite (a 20-fold excess) is used. Iodide should be added to the dilute nitrite solution to reduce the anomalies and when phenols or active methylene derivatives are present they should be treated with bromine before diazotisation.

E. KAWERAU

742. Chromatographic semi-micro analysis of gases. XI. Direct estimation of individual olefins. J. Janák and M. Rusek (Petroleum Res. Inst., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1955, **20** (4), 923-932.—Data are given for the chromatography of ethylene, propylene and butylene on silica gel B at 20°, 60° and 80° C. The optimum temp. for developing ethylene during chromatographic analysis is 20° C and that for propylene and butylene is 60° C. An apparatus is described for the absorption and concn. of olefin gases before chromatography when present at concn. of < 0.1 per cent. by vol. The absorbent employed is a 0.25 M Hg(ClO₄)₂ soln. in 2 M HClO₄. The vol. of sample is chosen so that the total vol. of olefins does not exceed 5 ml. The method enables individual olefins to be determined when present at concn. of $\approx 10^{-5}$ per cent. by vol. For concn. of olefins ≥ 0.1 per cent., an automatic gas circulator is incorporated into the apparatus, which allows a sample of 50 to 100 ml to be used directly. The accuracy of the method is $\approx 10^{-2}$ per cent. by vol.

J. H. WATON

743. Densities and refractive indexes for ethylene glycol - water solutions. E. T. Fogg, A. N. Hixson and A. R. Thompson (Univ. Pennsylvania, Philadelphia, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1609-1610.—Densities at 25° C and refractive indexes at 20° C were determined for mixtures of highly purified ethylene glycol and water. The density data provide a basis for analysis to within ± 0.11 per cent. by wt., and the refractive index data yield analyses accurate to within ± 0.03 per cent. by wt.

G. P. COOK

744. Polarographic determination of aldehydes as 2:4-dinitrophenylhydrazones. L. N. Petrova and E. N. Novikova. *Zh. Prikl. Khim.*, 1955, **28**, 219-221.—Aldehydes can be determined by indirect polarography by conversion into the 2:4-dinitrophenylhydrazones in ethanol, followed by polarographic determination of the unchanged 2:4-dinitrophenylhydrazine (I), which begins to reduce at 0.05 V with $E_1 = 0.2$ to 0.25 V vs. the S.C.E. The diffusion coefficient from the Ilković equation for I is 5.5×10^{-6} sq. cm per sec. The results are accurate within < 3 per cent. for aldehyde concn. of 0.6 to 1.5 millimoles per litre. CHEM. ABSTR.

745. Direct determination of acetic acid in acetic anhydride. J. H. McClure, T. M. Roder and R. H. Kinsey (E. I. du Pont de Nemours and Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1599-1601.—Two methods are described which are based on the reaction of triethylamine with the free acid in the anhydride. The first method is titrimetric; triethylamine in benzene is used as the titrant with methyl red as indicator. The second

method is thermometric, the temp. rise being measured as the reagent is added to the sample. A precision of ± 0.07 per cent. absolute is attained with the visual method over the range 0.5 to 3.5 per cent. of acid and 0.09 per cent. absolute for the thermometric method over the range 0.8 to 5.5 per cent. of acid. Application to other acids in acetic anhydride was successful, results being within the precisions quoted. Neither of the methods is applicable in the presence of amines.

G. P. COOK

746. Precise assay of trichloroacetic acid by coulometry at controlled potential. T. Meites and L. Meites (Yale Univ., New Haven, Conn., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1531-1533.—Trichloroacetate ion in ammoniacal medium is quant. reduced to dichloroacetate ion at a mercury cathode maintained at a constant suitable potential. Integration of the current flowing during electrolysis permits the determination of trichloroacetate ion in pure samples or in the presence of 8 times as much dichloroacetate ion, with an accuracy and precision within ± 0.2 per cent. The range covered was from 0.037 to 5.69 g of trichloroacetic acid.

G. P. COOK

747. Determination of calcium propionate. M. Bergmann. *Chem. Tech., Berlin*, 1955, **7** (8), 483.—The method described can be used for determining the calcium propionate in mixtures of calcium propionate and calcium diorthophosphate ($\approx 55:45$) as employed for adding to dough to prevent mould growth in bread. The method is suitable for control analysis in the manufacture of these mixtures. *Procedure*—The sample (1 g) is mixed with 1.5 g of CaCO₃, 100 ml of water are added, and the mixture is heated to boiling point. The product is cooled, the evaporated water is replaced, and the liquid is filtered. The clear filtrate (50 ml) is placed in a porcelain dish and neutralised with 0.5 N H₃PO₄, then an excess (e.g., 10 ml) of 0.5 N H₃PO₄ is added, the mixture is evaporated to dryness on the water bath, and the residue is heated to 150° C for 15 min. Water is added to the cooled residue and the excess of acid is back-titrated with 0.5 N NaOH. The difference obtained gives the amount of acid used to liberate the free propionic acid, and from this the amount of calcium propionate can be calculated. H. L. WHITEHEAD

748. A rapid method for the determination of reducing sugars by paper chromatography. H. Venner (Inst. Mikrobiol. und exp. Therapie, Jena). *Naturwissenschaften*, 1955, **42** (7), 179-180.—The circular technique is recommended and the best solvent mixture for rapid working was found to be butanol - acetone - aq. NH₃ - water (40:50:3:15). A sharp separation without tail formation was obtained after 45 minutes' running at room temperature. Aniline phthalate reagent is recommended for colour development and a comparison of colour intensities for quantitative appraisal. R_F values are given.

E. KAWERAU

749. Use of acid - base indicator for quantitative paper-chromatography of sugars. K. J. Gardner (Mars, Ltd., Slough, Bucks., England). *Nature*, 1955, **176**, 929-930.—The soln., e.g., 0.2 ml, containing up to 50 mg of total sugars, is applied to the centre of a Whatman No. 3 paper. The paper is dried, developed, dried again and then sprayed with an indicator of the following composition: 40 mg of bromocresol purple and 100 mg of boric acid

dissolved in 100 ml of methanol, to which 7.5 ml of 1 per cent. borax soln. are then added. Sugars are shown up yellow against a blue background and their position is marked immediately. The rings are cut out, and the sugars are eluted and then estimated by the compleximetric method of Potterat and Eschmann (*Anal. Abstr.*, 1955, **2**, 1327), which gives good results over the range 2 to 40 mg of sugar. Results are given for a pure glucose soln. and for a mixture of lactose and sucrose. The solvent *n*-propanol-ethyl acetate-water (6:1:3) is normally satisfactory, but four successive runs in formic acid-*n*-butanol-water (1:5:4) were necessary for separating glucose and fructose. O. M. WHITTON

750. Polarographic analysis of sugar tetrazolium derivatives and sugar formazans. B. Jámor and L. Mester (Inst. Plant Physiol., L. Eötvös Univ., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 263-273.—A polarographic study of the reduction of galactodiphenyltetrazolium chloride (I) indicates that there is no separation of the wave involving four electrons at any pH. The first and second steps in the reduction proceed in parallel, and only the rate at which each of the two steps participates varies with pH. Because of this, and because of the greater solubility of the formazan (II), I is reduced to the red II only in fairly strong alkaline soln.; the reduction is irreversible. The behaviour of I (and of its acetylation product) is compared with that of triphenyltetrazolium chloride, and their use as biological redox indicators is discussed. J. H. WATON

751. Determination of polysaccharides with thymol in sulphuric acid. C. J. Gomez and M. R. Gris. *Rev. Soc. Argent. Biol.*, 1955, **30** (6, 7 and 8), 276-288.—The samples are prepared as in Seifter's method (*Arch. Biochem.*, 1950, **25**, 191). Polysaccharide solution (0.06 ml) is treated with ethanol and the resulting ppt., after being centrifuged, is dissolved in 1 ml of 3 per cent. NaOH and made up to 10 ml. A 1 to 2-ml portion of this solution (made up to 2 ml with water) is cooled with ice for 5 to 10 min., then treated with 4 ml of a 0.2 per cent. solution of thymol in H_2SO_4 at $< 30^\circ C$. The product is heated at $100^\circ C$ for 10 min., cooled for 5 min., and the colour is read at 506 $m\mu$ (for hexoses and polysaccharides), or 490 $m\mu$ (for pentoses), against a blank. Mucoproteins are hydrolysed with $HClO_4$ and purified by tungstophosphoric acid pptn. before the determination. The colour is stable for several hours, and proteins do not interfere. The sensitivity is $\approx 5 \mu g$ of carbohydrate in 2 ml of solution, and the scatter of results is < 6 per cent. T. P. McLAUGHLIN

752. Colorimetric submicro-method for determination of ammonia. P. G. Scheurer and F. Smith (Univ. Minn., St. Paul, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1616-1618.—The blue colour produced by the action of phenol and $HOCl$ on NH_3 forms the basis for the determination of NH_3 in concn. as low as 8×10^{-8} mole per ml; the limit of detection is 5×10^{-10} mole per ml. The accuracy is ± 2 per cent. The method was used for the determination of the mol. wt. of compounds containing N that is easily transformed into NH_3 . G. P. COOK

753. Rapid determination of traces of iron and copper in acrylonitrile [vinyl cyanide]. R. L. Maute, M. L. Owens, jun., and J. L. Slate (Monsanto

Chem. Co., Texas City, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1614-1615.—In the colorimetric methods described the colour reactions and absorbance measurements are made in the vinyl cyanide phase; 2,2'-diquinolyl (cuproine) and *o*-phenanthroline are the reagents for Cu and Fe, respectively. Either metal can be determined in an excess over the other and there is no interference from a hundred-fold excess of CN^- . Reproducibility is within ± 0.03 p.p.m. and concn. as low as 0.05 p.p.m. can be determined. G. P. COOK

754. Routine determination of low-molecular-weight thiol compounds with sodium nitroprusside and cyanide. L. Rausch and K. Hamer (Münster Univ., Germany). *Klin. Wochschr.*, 1955, **33** (37-38), 899-900.—The reddish-violet colour produced by an alkaline soln. of sodium nitroprusside, enriched with NaCl, with a low-mol.-wt. thiol (e.g., glutathione) is stabilised by KCN. Reagents required are (i) 2 to 5 per cent. HPO_3 , preserved in a refrigerator for > 3 weeks, (ii) a hot saturated and filtered aq. soln. of NaCl, (iii) Na_2CO_3 (15.9 g) and KCN (50 mg) and water to 100 ml, (iv) sodium nitroprusside, a 2 per cent. freshly made (> 8 hr.) aq. soln.; all the reagents are made up in twice-distilled water. Methods of preparing extracts from blood or tissues and further experimental details for carrying out the colorimetric determination are described. P. HAAS

755. New reaction of thiourea. F. Hernández-Gutiérrez. *An. Real Soc. Esp. Fis. Quím.*, 1955, **51B** (6), 417-422.—An alkaline mercuri-iodide solution (0.1 *M* mercuri-iodide, 0.133 *M* alkali hydroxide) gives with an aq. solution of thiourea a yellow ppt. of a complex, the properties of which are in accordance with the constitution $Hg[SC(NH_2)_2:NH_2I]_2$; 4 μg per ml of thiourea may be detected. The pptn. is not quantitative, but the concn. of thiourea may be estimated photometrically, preferably with a blue filter, by calibrating with solutions of known concn. over the range 10 to 100 μg per ml. L. A. O'NEILL

756. Separation of thiourea and ammonium thiocyanate. Isamu Tsubaki and Mitsuo Kiboku (Osaka Ind. Sci. Res. Inst., Ikeda-shi, Osaka, Japan). *Japan Analyst.*, 1954, **3** (6), 478-481.—Reactions of thiourea and NH_4SCN with various metal ions were studied and it was found that thiourea is quant. pptd. with Hg^{++} at a pH > 4 , whereas NH_4SCN is not pptd. with Hg^{++} at a pH < 6 . A mixture of the two substances is treated with a saturated soln. of ammonium acetate (10 ml) and $HgCl_2$ (10 ml) and the pH is adjusted to between 4 and 6. The ppt. of the mercury compound of thiourea is decomposed with aqua regia and $KClO_3$ to convert all the S into sulphate, which can be determined with $BaCl_2$ by the usual method. Methods of detection of traces of NH_4SCN ($> 1 \mu g$ in 10 mg) in thiourea with $FeCl_3$ and of thiourea ($> 5 \mu g$ in 5 mg) in NH_4SCN with selenous acid are also suggested. K. SAITO

757. Quantitative method for the analysis of volatile and gaseous organosilicon compounds. H. Kautsky, G. Fritz, H. P. Siebel and D. Siebel (Marburg Univ., Germany). *Z. anal. Chem.*, 1955, **147** (5), 327-338.—An apparatus is described for the semi-micro determination of volatile and gaseous organosilicon compounds. After combustion, Si remains as SiO_2 in the combustion tube,

whilst H and O are determined by the usual methods. If a halogen is present, it is removed quant. by a boat containing powdered silver in an additional furnace placed between the combustion furnace and the tubes for absorbing water and CO_2 . With 30 to 40 mg of sample, the method gives an accuracy of ± 0.4 per cent. for Si, ± 0.3 per cent. for C, ± 0.2 per cent. for H and ± 0.2 per cent. for Cl.

J. H. WATON

758. Refractometric method of determining free alkali in phenoxides. A. K. Spitsyn and G. A. Markus. *Zavod. Lab.*, 1955, **21** (5), 570-574.—A modification of the formula of Lebedeva and Genshtein (*Zavod. Lab.*, 1952, **19**, 1442) gives

$$A = \frac{100}{n_{\text{ph}} - n_{\text{alk}}} n_m - \frac{100}{n_{\text{ph}} - n_{\text{alk}}} n_{\text{alk}}$$

where A is the percentage content of a phenol in an alkaline solution, n_m is the refractive index of the phenol-alkali mixture, n_{ph} is that of the pure phenol in solution, and n_{alk} is that of the pure alkali solution. Experimental data show that alkaline solutions with similar percentage contents of phenols, cresols and xylenols, and mixtures of phenols from medium-light and naphthalene oils have nearly the same refractive index. In phenol-alkali mixtures with similar alkali contents and in pure alkali solutions n_{ph} and n_{alk} are constants, then

$$\frac{dA}{dn_m} = \frac{100}{n_{\text{ph}} - n_{\text{alk}}} = \frac{A_2 - A_1}{n_{m_2} - n_{m_1}}$$

where n_{m_1} and n_{m_2} are the refractive indexes of solutions containing percentages A_1 and A_2 of phenol. For solutions of similar alkali content, experimental data show that $\frac{dA}{dn_m}$ is practically const. From the refractive indexes of a phenol solution containing free alkali and the same solution after neutralisation of the free alkali with phenol the concn. of free alkali can be calculated from the equation

$$C = \frac{M_1}{M_2} \times \frac{(n_2 - n_1) \frac{dA}{dn_m} \times 100}{100 - (n_2 - n_{\text{alk}}) \frac{dA}{dn_m}}$$

where M_1 is the mol. wt. of the alkali, M_2 is the mol. wt. of the phenols used for neutralisation, n_{alk} is the refractive index of the pure alkali solution, and n_1 and n_2 are the refractive indexes of the phenol solution before and after neutralisation.

G. S. SMITH

759. Colorimetric determination of catechol. S. D. Radosavljević, M. S. Jačović and M. D. Dragojević (Chem. Tech. Inst., Belgrade). *Bull. Soc. Chim., Belgrade*, 1955, **20**, 203-205.—A procedure is described for the quant. colorimetric determination of catechol in which the colour reaction of catechol in alkaline solution with FeCl_3 is used. The reaction may be applied to the determination of catechol in condensation products with methylchlorosilanes.

N. E.

760. Rapid colorimetric determination of benzidine. R. G. Rice and E. J. Kohn (Naval Research Lab., Washington, D.C., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1630-1631.—Benzidine is oxidised by MnO_4^- in the presence of HNO_3 to produce a greenish-yellow colour whose intensity, on dilution, conforms to Beer's law. The average deviation between results from this method and a gravimetric procedure is ± 0.19 g per litre for soln. containing 19 to 25 g of benzidine dihydrochloride per litre. The average precision for duplicate

determinations is ± 0.13 g per litre. Reproducibility is unaffected by small quantities of HCl.

G. P. COOK

761. Identification of iminazole compounds by paper chromatography. R. W. Cowgill (Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1519-1521.—A paper-chromatographic method in which three solvent systems are used, singly or in combination, is described for the identification of 20 iminazole compounds. The identity of the spots is further established by their appearance with u.v. light, a *p*-phenyldiazonium sulphate spray or an iodine spray; the iodine spray reveals the location of 1-substituted iminazole compounds.

G. P. COOK

762. Iodimetric method for the determination of 8-hydroxyquinoline in the presence of copper. M. R. Verma and V. M. Bhuchar (National Physical Laboratory of India, New Delhi). *J. Sci. Ind. Res., B, India*, 1955, **14** (8), 419-421.—In the volumetric determination of Cu as its oxinate, by a method similar to that for Cd, Zn, etc., interference is caused by the liberation of I by Cu^{++} in addition to the iodine equivalent of excess of Br. This is avoided by complexing the Cu with K citrate or EDTA (disodium salt). For example, to a known vol. of oxine soln. is added CuSO_4 soln. and Na acetate; a yellow-green ppt. is formed. To the mixture are added KBr, standard KBrO_3 soln. and H_2SO_4 . After 10 min., KI is added, and the combined I, equivalent to the unchanged Br and Cu^{++} , is liberated. To the soln. are added 20 ml of M K citrate (free from reducing substances) and the pH is cautiously raised to 6.2 by adding alkali. Cuprous iodide recombines with I to give Cu^{++} , which are complexed by the K citrate. The free I is now equivalent to the Br in excess of that required for bromination of the oxine. From the titration values, the Br combined with the oxine, and hence the oxine, can be determined.

I. JONES

763. Researches into the synthesis and determination of tropinone. G. Gál, I. Simonyi and G. Tokár (Lab. United Pharm. and Nutrient Factory, Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 365-371.—Tropinone is pptd. quant. by Reinecke's salt, when a pink tropinone reineckate of composition $\text{C}_8\text{H}_{13}\text{ONH}[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]$ is formed. A 20 to 30 per cent. excess of a 1 per cent. filtered aq. soln. of Reinecke's salt is used, so that the supernatant liquid remains pink. After dilution, the ppt. is allowed to stand for 1 hr., when it is filtered through a No. 3 sintered-glass filter. The ppt. is washed first with water and then twice with 5 ml of 96 per cent. ethanol and dried for 30 min. at 105°C .

J. H. WATON

764. Accelerated lamp method of determining sulphur in various petroleum products. N. P. Volynskii. *Zavod. Lab.*, 1955, **21** (5), 536-539.—A modification of the lamp used is described. It consists of a heat-resistant glass oblate spheroid fused to a capillary, which slopes downwards and is turned up at its end to form the orifice for insertion of an asbestos wick. Between the reservoir and the capillary is a small bulb, which initially holds dioxan used for heating the wick and for the purpose of regulating the flame.

G. S. SMITH

765. Determination of very low concentrations of hydrogen sulphide in gas. I. C. G. T. Prince (North Thames Gas Board, Fulham Works,

London). *J. Appl. Chem.*, 1955, **5** (8), 364-374.—In an investigation of various methods of determining low concentrations of H_2S in gas, the methylene blue method was calibrated by a modified method and its accuracy verified volumetrically and gravimetrically. It was then used as a primary standard to determine the relation between extinction and the sulphur content of PbS stains resulting from the passage of gas through absorbent paper impregnated with Pb acetate, the stain density being measured by a specially designed photoelectric densitometer. S.C.I. ABSTR.

766. Microchemical reaction for the differentiation of synthetic fibres. W. Kunze. *Reyon Zellwolle Chemiefasern*, 1955, (6), 386-387.—A soln. of diphenylamine in conc. H_2SO_4 (10 mg in 100 ml), to which one drop of cold saturated $CuSO_4$ soln. was added, was found to be a suitable micro-reagent for the identification of poly(vinyl cyanide) fibres, which begin to dissolve in the reagent after 30 to 45 sec. with gradual development of a blue coloration. With polyester fibres this reaction is negative. For their identification they are boiled with alcoholic KOH or NaOH to split them into terephthalic acid and glycol. The terephthalic acid can be pptd. in cryst. form by carefully acidifying, and identified from its cryst. sublimate, which is insol. in ether, acetic acid, chloroform and cold ethanol. The glycol and formaldehyde formed can be identified.

BRIT. COTTON IND. RES. ASS. ABSTR.

767. A note on the use of benzene-acetic acid-water as an eluent in the separation of phenol-formaldehyde condensates by paper chromatography. H. G. Peer. *Rec. Trav. Chim. Pays-Bas*, 1955, **74** (6), 793-794.—Phenol-formaldehyde condensates are separated into their intermediates, according to the no. of phenol rings per mol., by a CO_2 -water eluent; these fractions are then separated into components, according to the number of *o*-hydroxy groups in the mol., by a mixture of benzene, acetic acid and water (20:8:2, by wt.). The composition of the mixture is somewhat critical.

E. J. H. BIRCH

768. Determination of monomer in poly(vinyl acetate). Yuji Takayama (Mitsubishi Rayon Co., Kyobashi, Tokyo, Japan). *Japan Analyst*, 1955, **4** (5), 299-302.—An ester of a monobasic aliphatic acid and hydroxylamine interact in light petroleum to produce an equiv. amount of hydroxamic acid, which gives a violet colour on the addition of ferric ion. This reaction is applied to the determination of the monomer in poly(vinyl acetate). The polymer can undergo a similar reaction to a less extent and should be removed before the addition of the reagents. *Procedure*—The sample (0.1 to 5 per cent. of monomer) (10 to 50 mg) is dissolved in toluene (0.5 ml) and treated with light petroleum (4 ml) to ppt. the polymer. The supernatant liquid is decanted into another stoppered vessel and the residue is washed with several portions of light petroleum (0.5 ml). The washings are combined with the supernatant liquid and treated with NaOH (2.5 per cent. in ethanol) (1 ml) and hydroxylamine hydrochloride (2.5 per cent. in ethanol) (1 ml) at 20° C for 10 min. and then at 55° C for 16 min. The product is made up to 25 ml with $FeCl_3$ soln. (10 ml) and methanol, and the extinction is measured at 530 $m\mu$. For the prep. of the iron soln., Fe (0.4 g) is dissolved in HNO_3 (1 + 1) (30 ml) and heated with $HClO_4$ (60 per cent., 20 ml)

until fumes of $HClO_4$ are evolved, when water (30 ml), conc. HNO_3 (10 ml) and $HClO_4$ (60 per cent.), to a vol. of 100 ml, are added. One ml of this soln. is mixed with 100 ml of ethanol immediately before use. K. SAITO

769. Determination of benzoyl peroxide in poly(methyl methacrylate). II. Ultra-violet absorption spectroscopy. Yuji Takayama (Mitsubishi Rayon Co., Kyobashi, Tokyo, Japan). *Japan Analyst*, 1955, **4** (5), 290-293.—The extinction coefficient of benzoyl peroxide (**I**) at 276 $m\mu$ is proportional to the concn. within the range 1 to 5 $\times 10^{-3}$ M in $CHCl_3$, the specific extinction being 2.36×10^3 ; those of the methyl methacrylate monomer and polymer are 7.5 and 1.0, respectively. **I** (0.1 to 1 per cent.) in poly(methyl methacrylate) which contains 0.2 to 0.5 per cent. of the monomer can be rapidly analysed by measurement of the extinction in a $CHCl_3$ soln. of the sample (0.1 g in 10 ml). The extinction due to the absorption of methacrylate polymer and monomer is subtracted from the observed value and the amount of **I** is calculated. A similar method can be applied to the determination of tetralin peroxide in poly(methyl methacrylate). K. SAITO

770. Polarographic determination of phthalic anhydride in alkyl resins. P. D. Garn and E. W. Halline (Bell Telephone Lab., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1563-1565.—The sample is saponified and the pptd. potassium phthalate is dissolved in dil. H_2SO_4 . The diffusion current of this soln. is measured on the polarograph with tetramethylammonium bromide as the inert electrolyte. Phthalic acid gives a well-defined wave at -1.08 V vs. the S.C.E., and the diffusion coefficient is 8.6×10^{-6} sq. cm per sec. for this solvent. Recoveries are good. Interference from maleic or fumaric acids may be eliminated by a controlled-potential electrolysis. Application to commercial samples gave results in close agreement with those from gravimetric techniques.

G. P. COOK

771. Determination of mixed phthalic acid isomers in alkyl resins. M. H. Swann, M. L. Adams and D. J. Weil (Aberdeen Proving Ground, Md., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1604-1606.—In the determination of the three isomers of phthalic acid the acids are recovered from the resin soln. with a special saponification technique and are then hydrolysed in methanol soln. Absorptivity measurements at 275, 281 and 287 $m\mu$ are made, from which the concn. of the individual isomers are calculated. The accuracy for the *o*- and *p*-isomer determination is ± 1 per cent. and for the *m*-isomer $\approx \pm 1.5$ per cent. G. P. COOK

772. Chlorine determination in chlorine-containing plastics. I. Ubaldini and F. C. Maitan (Istituto di Chimica Industriale del Politecnico, Milan). *Chim. e Ind.*, 1955, **37** (10), 779-781.—The determination of chlorine in chlorine-containing resins and plastics and other organic substances of low volatility can be performed exactly and conveniently by Eschka's method, by calcination with a mixture of magnesium oxide and dry sodium and potassium carbonates, followed by determination of the alkali chloride, either by Volhard's method or with mercapto-benzothiazole. The former method is preferable for materials with a high- or medium-chlorine content, the latter method for materials containing only

small amounts of chlorine. Results of several typical determinations are reported.

C. A. FINCH

773. Determination of free sulphur in hard rubber. C. Wynne-Evans (Dunlop Rubber Co. Ltd., Manchester, England). *I.R.I. Trans.*, 1955, **31** (4), 126-131.—Free S in ebontite (from natural or synthetic rubber, or reclaim) is estimated by the extraction of the finely ground material with Na_2SO_3 solution and titration of the $\text{Na}_2\text{S}_2\text{O}_3$ formed, with I. Hard rubber filings (2 g, to pass 12 mesh, retained on 22 mesh) are extracted at the b.p. for 3 hr. with 100 ml of 5 per cent. Na_2SO_3 solution and 5 ml of 0.1 per cent. Na stearate solution, in the presence of 1 g of paraffin wax. The Na stearate, a wetting agent, facilitates extraction of the S, but causes frothing, which the wax reduces. A 0.5 per cent. SrCl_2 solution (100 ml) is added, together with 10 ml of 3 per cent. Cd acetate solution (unless mercaptobenzothiazole is known to be absent), followed by separation of the ppt. by vacuum filtration and washing with two portions (75 to 100 ml) of Cd acetate solution (40 ml of 3 per cent. Cd acetate solution per litre). To the filtrate are added 5 ml of 40 per cent. formaldehyde solution, 10 ml of glacial acetic acid and 5 ml of 1 per cent. "thiodene" indicator, together with sufficient crushed ice to bring the temp. to 15° C; titration is then effected with iodine solution.

J. L. PROSSER

774. Absorptiometric micro-determination of total sulphur in rubber products. K. E. Kress (Firestone Tire and Rubber Co., Akron, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1618-1624.—The sulphur in rubber products is oxidised to SO_4^{2-} with conc. HNO_3 -Br reagent and HClO_4 in the presence of excess of $\text{Pb}(\text{NO}_3)_2$. The ppt. PbSO_4 is washed with acetone and dissolved in HCl, and the extinction of the PbCl_2 complex is measured at 270 μ . Recovery of added S was 97 to 108 per cent. and the mean deviation for three samples was between ± 0.02 to ± 0.06 per cent. Results were in good agreement with those from a gravimetric procedure.

G. P. COOK

775. Determination of sulphur in rubber vulcanisates. E. W. Zimmerman, V. E. Hart and E. Horowitz (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1606-1609.—A combustion method for rubber, by which the S evolved at 480° to 500° C is determined, is compared with the fusion and zinc- HNO_3 methods. In the combustion method, interaction between the S and the fillers present in the rubber often renders an inaccurate value and the effect of various fillers is discussed. The fusion method gives results in good agreement with the total S added in compounding the rubber samples; the Zn- HNO_3 method also determines total S, except in the presence of Ba. The standard deviations for the fusion and Zn- HNO_3 methods are 0.1 and 0.09 per cent., respectively.

G. P. COOK

776. Identification of accelerators and antioxidants in compounded rubber products. M. J. Brock and G. D. Louth (Firestone Tire and Rubber Co., Akron, Ohio, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1575-1580.—The extraction technique described promotes the tendency for accelerators to decompose during mixing, vulcanisation or extraction from compounded stocks. The accelerator

components thus obtained are separated by extraction and distillation, and their identification enables the identity of the accelerators to be determined. Amine antioxidants remain unchanged and are identified by u.v. absorption and colour tests. Most of the commonly used accelerators and antioxidants can be classified or identified, and the method also includes provision for possible future antioxidants and accelerators.

G. P. COOK

777. Analytical determination of some elastomeric components in aqueous extracts. K. Marcali (E. I. du Pont de Nemours and Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1586-1593.—Analytical methods are described for the determination of traces of Zn, phenothiazine, 4-tert.-butylcatechol, a disproportionated rosin, sodium salts of condensed mononaphthalenesulphonic acid and anthraquinone-2-sulphonic acid in aq. extracts from elastomers. The first four components are measured colorimetrically and the last two by simultaneous spectrophotometry. The mean recovery at the 2 p.p.m. and 20 to 50 p.p.m. level for all the methods was $> \approx 96$ per cent., and reliable detection of < 0.5 p.p.m. was also achieved.

G. P. COOK

See also Abstract 897.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

778. Determination of serum calcium. A comparison between the method of Clark and Collip and the titration with ethylenediaminetetra-acetate. L. Eldjarn, O. Nygaard and S. L. Sveinsson (Norwegian Radium Hosp., Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1955, **7** (1), 92-94.—The EDTA (disodium salt) method (I) gave, on the average, lower values than Clark and Collip's method (II) (*J. Biol. Chem.*, 1925, **63**, 461). The best agreement was obtained by multiplying the I values by a factor 1.046 (standard deviation ± 0.030). For II the average range for 82 sets of duplicates was 0.09 mg per cent. and for I the range for 61 sets was 0.120 mg per cent.; the reproducibility of the two methods is thus approx. the same. I was found to be, on the average, twice as quick as II, the result being given in 5 to 10 min. A diagram of a modified arrangement for the titration of Ca by I is given.

P. HAAS

779. A simple colorimetric determination, suitable for routine examination, of bismuth in urine. E. Flotow (Bezirks-Hygiene-Institut, Dresden, Germany). *Pharm. Zentralh.*, 1955, **94** (5), 178-179.—To 50 ml of urine in a 250-ml Kjeldahl flask add conc. H_2SO_4 (2 ml), conc. HNO_3 (5 ml) and digest, adding further small quantities of HNO_3 as necessary until the solution is colourless. Dilute to 10 ml and remove any ppt. by centrifuging. To an aliquot (5 ml) add 6 drops of NaHSO_4 solution (1 per cent.), shake and add 5 drops of KI solution (20 per cent.). Compare the yellow colour with that from standard bismuth solutions after from 15 min. to 2 hr. The method is unsuitable for the determination of Bi in whole blood as Fe interferes, but it is suitable for the determination of Bi in plasma.

P. S. STROSS

780. Determination of iron and copper in serum. G. Zausch (Bacteriological Inst. Behring Hospital, Berlin, Germany). *Klin. Wochschr.*, 1955, **33** (39-40), 954-956.—A number of improvements in Heilmeyer's method are suggested. (1) Adjustment of the soln. to pH 2, in determining Fe colorimetrically by phenanthroline and 2:4-dinitrophenol, increases the depth of colour and reduces sensitivity to small deviations in pH. The max. colour is reached only after 1 hr., thus leaving sufficient time for calibration of a standard soln. (2) In determining Cu by means of the sparingly soluble Cu-carbamate complex, turbidity is eliminated during the colorimetric measurements by shaking with amyl alcohol, which is insol. in water, in preference to ethanol; this has the effect of stabilising the Cu-carbamate complex and causing an increased concn. and consequent greater depth of colour; further, the uncertain removal of Fe with pyrophosphate above pH 8 is no longer necessary. P. HAAS

781. Polarographic detection of ethanol [in biological fluids]. O. Schmidt and R. Manz (Univ. Inst. of Forensic Med., Göttingen, Germany). *Klin. Wochschr.*, 1955, **33** (35-36), 857-863.—Oxidation of ethanol to acetaldehyde is carried out in a special Plexiglas diffusion apparatus (*cf. Ibid.*, 1955, **33**, 82). Methanol does not affect the method, and other biological substances that yield either ethanol or methanol should be previously eliminated by the removal of protein with 3.3 per cent. HClO_4 . The range of variation in the determination of ethanol in aq. soln. is ± 1 per cent. The oxidising agent is a 5 per cent. soln. of $\text{K}_2\text{Cr}_2\text{O}_7$ in 0.5 N H_2SO_4 containing 0.5 g of CrCl_3 . The acetaldehyde produced is absorbed by LiHSO_3 (prepared by saturating Li_2CO_3 with SO_2), to give a stable bisulphite compound. This, on treatment with LiOH , liberates acetaldehyde, which is determined polarographically. Numerical data and calibration curves are given. P. HAAS

782. Separation of mixture of nine monosaccharides by two-dimensional ascending paper-chromatography. D. Hamerman, K. W. Bartz and A. Reife (Fitzsimons Army Hospital, Denver, Colo., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1524-1525.—A mixture of rhamnose, fucose, ribose, xylose, arabinose, fructose, mannose, glucose and galactose was resolved and the components were separated from two hexuronic acids by a two-dimensional ascending chromatographic method. The first run was made with a mixture of *n*-butanol, pyridine and water (3:2:1.5), and the second with phenol saturated with water. Characteristic colours were obtained by spraying with 2-naphthylamine. G. P. COOK

783. Spectrophotometric determination of creatinine in alcoholic solution. L. Jacobsson and L. Paulsen (Sahlgren's Hosp., Göteborg, Sweden). *Scand. J. Clin. Lab. Invest.*, 1955, **7** (1), 32-34.—Creatinine was dissolved in various solvents and the absorption in the u.v. region was recorded in a Beckman DU spectrophotometer, light-path 1 cm. In methanol-water (4+1) and ethanol-water (4+1) and in pure butanol a distinct max. in the u.v. region was obtained at 235 to 236 m μ . No max. was obtained with creatinine in the same solvents. A standard curve for creatinine in ethanol-water (4+1), which obeys the Beer-Lambert law, is given. P. HAAS

784. Noradrenaline and adrenaline in urine. I. Chemical determination. A. Pekkarinen and M. E. Pitkänen (Univ. Helsinki, Finland). *Scand. J. Clin. Lab. Invest.*, 1955, **7** (1), 1-7.—Adrenaline (I) and noradrenaline (II) can be adsorbed from urine on to alumina at pH 8.5, and eluted from the oxide by oxalic acid at pH 3, which simultaneously precipitates calcium salts. I and II are oxidised by MnO_2 to adreno- and noradreno-chrome and their fluorescence is developed by 5 N NaOH. To distinguish between I and II, the fluorescence of the eluate is determined first in alkaline soln. and then after oxidation with MnO_2 ; the fluorescence of II develops later and is much less intense than that of I. At the time of max. fluorescence of I, that of II is only 1 to 2 per cent. of the amount observed after oxidation. By this method 75 to 80 per cent. of I and II can be recovered. P. HAAS

785. A new simple method for the determination of isoniazid in body fluids. H. Harting and P. V. Gerzanits (Chemische Fabrik Harting y Cia, Santiago). *Acta Med. Biol.*, 1954, **2** (3), 643-648.—Isoniazid may be determined in urine, blood, pleural exudate, etc., by oxidation with excess of alkaline ferricyanide and measurement of the volume of N liberated. Proteins, amino acids, urea and uric acid do not interfere, and the determination may be carried out on coloured or turbid soln., but thiosemicarbazones must be absent. *Procedure*—Mix the sample (*e.g.*, 50 ml of urine) with 20 per cent. NaOH (5 ml) in one limb of a bifurcated flask, add 20 per cent. $\text{K}_3\text{Fe}(\text{CN})_6$ (10 ml) to the other limb, and connect to a gas burette. Tilt the flask to mix the liquids, and when reaction is complete read the volume of gas liberated. A. R. ROGERS

786. Detection of drugs of addiction in urine by means of high-tension electrophoresis. Isamu Sano and Harutoshi Kajita (Universitäts Nervenkl., Osaka, Japan). *Klin. Wochschr.*, 1955, **33** (39-40), 956-958.—Because of certain imperfections in Jatzkewitz's paper-chromatographic method for detecting basic drugs of addiction, Heilmeyer's high-tension electrophoresis method (*cf. Anal. Abstr.*, 1954, **1**, 3061) was used. A 10 per cent. soln. of acetic acid was used as a buffer for the 17 basic substances separated; these included methylamphetamine, procaine, diphenhydramine, codeine, cocaine, morphine, ethylmorphine and diamorphine. During a 20-min. run, 11 of the drugs did not differ very much in their migration rate, but after 35 min. there was a satisfactory separation. Particulars are given of the various reagents used for developing the bases. Methylamphetamine was detected in urine in microgram traces after 1 hour's run. P. HAAS

787. Spectrophotometric determination of pyruvic acid by the salicylaldehyde method. S. Bernström (Chalmers Tekniska Högskola, Göteborg, Sweden). *Anal. Chem.*, 1955, **27** (10), 1659-1660.—The method is a modification of that by Straub (*Hoppe-Seyl. Z.*, 1936, **244**, 117). The relative error in the range 0.0005 to 0.01 milli-equiv. is < 2 per cent. G. P. COOK

788. Paper chromatography of uronic acids. R. A. Edington and E. Percival (Univ. Edinburgh, Scotland). *J. Chem. Soc.*, 1955, 3554-3555.—Suitable solvent mixtures are butanol-acetic acid-water (40:10:50) and butanol-formic acid-water (500:115:385) which have been aged by

keeping at room temp. for 14 days or boiled under reflux for 1 hr. before use. The formic acid system is faster and less likely to cause badly shaped spots or trails than systems containing acetic acid. Aqueous aniline oxalate and butanolic *p*-anisidine hydrochloride are the most useful spray reagents; these give a brown or reddish-brown colour with uronic acids having a free OH group at C₍₁₂₎ and a red or purple colour with acids substituted at C₍₁₂₎. The colours and *R_F* values (reference sugar tetramethylglucose) of various uronic acids are tabulated.

H. F. W. KIRKPATRICK

789. Reliable and rapid determination of amino acids in protein hydrolysates. V. Mareček (Oils and Fats Res. Inst., Prague, Czechoslovakia). *Českosl. Farmac.*, 1955, **4** (7), 339-342.—The method based on chromatographic adsorption of hydrolysates is discussed. The chromatograms vary in intensity and size of the developed spots however carefully the conditions are controlled. This was found to be due to a number of factors, mainly the continual change in the composition of the hydrolysates. The nitrogen content of the soln. was determined and the chromatographic results were corrected to agree with it. Several hydrolyses have to be carried out under different conditions (excess of acid, temp. and reaction time) and the developed chromatograms are compared with standards. If the measurements are carried out spectrophotometrically an overall accuracy of ± 3 per cent. is obtained, whereas visual evaluation is correct to only ± 10 per cent. The quant. determination of individual amino acids is accurate to ± 15 per cent. Experimental details of the nitrogen determination (NH₃, primary amino, and total nitrogen), extent of hydrolysis, influence of reaction time and temp., and determination of individual amino acids are given.

A. O. JAKUBOVIC

790. The estimation of β -hydroxy amino acids by a micro-diffusion method. L. Wiseblatt and W. B. McConnell (Prairie Regional Lab., National Research Council of Canada, Saskatoon, Saskatchewan). *Canad. J. Chem.*, 1955, **33** (9), 1452-1453.—A method is described for determining "periodate ammonia" in protein hydrolysates in which Conway micro-diffusion units are used. *Reagents*—(A) 0.5 M H₂IO₆, (B) 5 per cent. glycine in N NaOH, (C) 5 N KBO₃ and (D) 2 per cent. H₂BO₃ containing 0.1 per cent. of a mixture of bromocresol green and methyl red (2:1). *Procedure*—In the centre well of a No. 1 Conway unit are placed 1.5 ml of D, and 1 ml of sample, containing about 10 microequiv. of β -hydroxy amino acids, followed by 0.5 ml of A, 0.5 ml of B and 1.5 ml of C, are placed in the outer chamber. The cell is sealed immediately and, after at least 5 hr., the contents of the centre are titrated with standard HCl. "Preformed NH₃" to be subtracted, is determined in a control experiment in the absence of A. The method gives an error of < 0.5 per cent. for pure serine (I) and threonine (II). In a protein hydrolysate, II can be determined separately by Winnick's method, and I found by difference, though hydroxyllysine, glucosamine or ethanolamine interferes if present. This method enables I and II and total N to be determined in samples of edestin, casein, ovalbumin and gluten, and the results agree with those previously reported.

A. B. DENSHAM

791. Colorimetric method for analysis of histidine and certain related iminazole compounds. R. W. Cowgill (Univ. Calif., Berkeley, U.S.A.). *Anal.*

Chem., 1955, **27** (10), 1521-1523.—Histidine and certain related iminazole compounds are determined by measuring the intensity of colour produced by their degradation with *p*-nitrobenzoyl chloride in alkaline soln. The method is capable of detecting 0.1 μ mole of histidine with a colorimeter and 0.025 μ mole spectrophotometrically at 417 m μ ; the standard deviation is ± 5.0 per cent. Hydrazine and hydroxylamine interfere, but phenols and aromatic bases, which interfere in other methods for histidine, do not, unless present in relatively large amounts.

G. P. COOK

792. Chromatographic separation of various iodo-amino acids by means of buffered volatile solvents. Application to iodine-containing constituents of the thyroid gland. J. Roche, R. Michel and J. Nunez (Lab. Biochim., Coll. France, Paris). *Bull. Soc. Chim. Biol.*, 1955, **37** (7-8), 809-817.—Buffered, completely volatile solvents have been adapted to the separation of amino acids of closely allied isoelectric points, such as various natural iodothyronines (thyroxine, 3:5:3'- and 3:3':5'-tri-iodothyronine and 3:3'-di-iodothyronine). The solvents used are (a) ethanol (95 per cent.) (1 pt.), 0.2 M ammonium carbonate (0.5 pt.) and 0.2 M ammonium acetate (0.5 pt.), pH 7.4, (b) ethanol (95 per cent.) (1 pt.) and 0.2 M ammonium carbonate (0.5 pt.), pH 7.8, and (c) pure methanol (1 pt.) and 0.2 M ammonium acetate (2.5 pt.), pH 6.2, with Whatman No. 1 paper for ascending chromatography. Three reagents were used for development: (i) ninhydrin, which detects 15 to 40 μ g of amino acids, (ii) Pauly's reagent (diazotised sulphanilamide) for 20 to 50 μ g of compounds containing a phenolic group and (iii) Bowden and MacLagan's Ce(SO₄)₂ and sodium arsenite reagent, which detects 0.5 to 4 μ g of all iodine compounds concerned; for > 0.2 μ g of I, ¹³¹I-labelled I was used. The buffered solvents used have the advantage of being completely volatile, and their saline constituents can be removed from the eluates by gentle heating or in a desiccator. By using two solvents in succession on the same spot the method can be adapted for use in place of two-dimensional chromatography.

P. HAAS

793. Normal values of paper electrophoresis and their evaluation according to the methods of Grassmann and Hannig, and of Turba and Enekel, and the possibility of comparing the two methods. W. Fuchs and A. Flach (Rheumatism Clinic Lab., Bad Bramstedt, Germany). *Klin. Wochschr.*, 1955, **33** (37-38), 903-906.—The authors were unable to reproduce the results for the normal values of human serum obtained by Grassmann and Hannig (*Ibid.*, 1954, 838, and earlier papers). The method of Turba and Enekel (*Naturwissenschaften*, 1950, **37**, 93) gives the results most closely resembling the normal values quoted in the paper. The discrepancies between the two methods are too large to make a comparison possible.

P. HAAS

794. Quantitative paper-electrophoresis of serum proteins. A contribution to its standardisation. E. J. van Kampen and H. A. Zondag (Klin.-Chem. Lab. Diakonessenhuis, Groningen, Holland). *Chem. Weekbl.*, 1955, **51** (29), 535-543.—The causes for discrepancies between results obtained by different workers using paper electrophoresis for the determination of protein in human serum are discussed, and a standardised method to eliminate such discrepancies is proposed. This method follows Grassmann's procedure (*Naturwissenschaften*, 1950,

37, 496) but conditions are defined in detail. Satisfactory agreement with results obtained by other procedures ["free" electrophoresis and salting-out with Na_2SO_4 (261 g per litre)] was achieved. The apparatus used consists of a rectifier, electrophoresis bath, scanner and an applicator to achieve even distribution of the serum on the paper. The equipment is described in detail and illustrations and photographs are given. *Procedure*—Saturate a paper strip (35 cm \times 5.1 cm) with buffer (pH 8.8) (1.0 g of barbitone and 10.3 g of Na barbitone). Remove excess of buffer solution, add about 0.04 ml of azocarmine-dyed serum from a pipette and distribute evenly. Subject the strip to reverse current (10 min.) and to electrophoresis, 0.25 mA being used per 1-cm width of paper, for 11 to 12 hr. Dry the strip at 105° C (5 to 10 min.), dip into a dye-bath (50 ml of methanol, 10 ml of glacial acetic acid, 0.75 g of azocarmine B, and H_2O to 100 ml) for 10 min., wash with 10 per cent. acetic acid and dry at 105° C. Five coloured zones appear. To make them transparent for quantitative measurement in the scanner, treat the zones with a mixture of equal parts of paraffin oil and 1-bromonaphthalene and expel air by placing in a vacuum-desiccator. Results are tabulated and, by comparison with "free" electrophoresis and salting-out with Na_2SO_4 , they are found to be sufficiently accurate for clinical use. Applications of this method to diagnosis are discussed. Coloured strips and curves obtained with normal and pathological sera are reproduced.

H. A. FISHER

795. A simple rapid method for the estimation of albumin and alpha-, beta- and gamma-globulins in serum. J. C. Aull and W. M. McCord. *J. Lab. Clin. Med.*, 1955, **46** (3), 476-483.—The method described is based on the photo-electric measurement of the turbidities produced when aliquots of a dilution of the serum under test are mixed with different dilutions of a 3.33 M phosphate buffer, pH 6.3. With decreasing buffer concentrations the apparent optical densities, or optical density differences, are proportional to total protein, albumin or the three individual globulins. Statistical comparisons of results by the proposed method are made with those given by the chemical method of Wolfson *et al.* (*Amer. J. Clin. Path.*, 1948, **18**, 723), and the differences are discussed.

W. H. C. SHAW

796. Spectrophotometric analysis of uncontaminated blood for oxyhaemoglobin. W. E. Huckabee. *J. Lab. Clin. Med.*, 1955, **46** (3), 486-493.—In the simple rapid method described, 1.5 ml of blood obtained anaerobically in polyvinyl tubing is haemolysed by freezing in a bath of acetone and solid CO_2 and thawing in a water bath at room temperature. The treated sample is then filled into 3- or 5-mm cells and the extinction at 660 m μ is measured against an arterial or saturated blood sample as blank. The reliability of the method is at least equal to that of gasometric methods.

W. H. C. SHAW

797. Comparative investigations of quantitative determination of protein in cerebrospinal fluid and in solutions of low protein content. M. Eggstein and F. H. Kreutz (Univ. Med. Clinic, Marburg, Germany). *Klin. Wochschr.*, 1955, **33** (37-38), 879-884.—Folin's copper method as modified by Lowry *et al.* (*Brit. Abstr. C*, 1952, 160) gives results in good agreement with those of the chemical determination by Kjeldahl. A 0.1-ml sample of

cerebrospinal fluid suffices for the determination. The ease and great accuracy of the method render it suitable for use in clinical laboratories; as little as 10 μ g of protein can be determined. Dittlebrand's method (*Amer. J. Clin. Path.*, 1946, **18**, 439) requires < 0.5 mg of protein and gives results 10 to 20 mg per cent. higher than does the chemical method, due in part to the reduction of the reagent by sugar contained in the cerebrospinal fluid. The xanthoproteic method gives results which are less accurate than those of the other two; on an average they are 9 mg per cent. too low. Formulae to aid the calculation of statistical results are provided. P. HAAS

798. Determination of alpha-ketolic substances in urinary extracts and paper chromatograms. J. C. Touchston and C.-T. Hsu (Univ. Pennsylvania, Philadelphia, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1517-1519.—The α -ketols were extracted from the urine with CHCl_3 and an aliquot was added to a paper strip, which was then sprayed with blue tetrazolium reagent. The colour was eluted with a mixture of ethyl acetate and methanol and was measured absorptiometrically. Recoveries of added α -ketolic steroids averaged 97 per cent. and duplicates showed an average deviation from the mean of 6 per cent. A study was made of normal, pregnancy and cortical carcinoma urines, the results of which are listed.

G. P. COOK

799. Quantitative determination of urinary pregnanediol and allopregnanediol for clinical use. C. C. Jensen (Women's Clinic, Malmö, Sweden). *Acta Endocrinol.*, 1955, **18**, 281-287.—Mix 2.5 per cent. of a 24-hr. urine sample with an equal vol. of toluene and heat under reflux to boiling point. Add 10 per cent. of the vol. of HCl, continue to boil the soln. for 10 min. then cool rapidly to 0° C. Shake the soln. well, wash the toluene twice with 20 ml of 4 N NaOH and 3 times with H_2O , and dry with Na_2SO_4 . Filter, evaporate *in vacuo* at 80° to 90° C and dissolve the residue in 0.5 ml of ethanol. Add 3 ml of 3 per cent. H_2O_2 and 0.25 ml of 2 per cent. NaHCO_3 soln. Heat for 4 min. at 100° C and keep at room temp. for 1 hr. Filter through a sintered-glass filter (15 to 40- μ pore size), wash 3 times with 10 ml of H_2O and wash the filter twice with 10 ml of boiling ethanol. Evaporate to dryness at 60° C in a stream of air, dissolve the residue in 5 ml of conc. H_2SO_4 , transfer after 1 hr. to a cuvette and determine the extinction at 415 and 530 m μ . The amount of pregnanediol in mg per 24 hr. is derived from the E_{415} value noted for 0.2 mg of allopregnanediol. The result is corrected for that part representing the absorption of non-specific substances by means of the ratio E_{530}/E_{415} . The correction factor is obtained from a curve supplied. From 10 μ g of allopregnanediol 83 to 99 per cent. could be found.

CHEM. ABSTR.

800. Determination of oestrogens by fluorescence after paper-chromatographic separation. A. Puck (Bonn Univ., Germany). *Klin. Wochschr.*, 1955, **33** (35-36), 865-867.—The author has developed a unidimensional ascending paper-chromatographic method of separating oestrogenic hormones, based on that of Bush (*Brit. Abstr. C*, 1952, 107), with the solvent benzene-methanol-water (5:4:1). The R_F values for oestrone, oestradiol and oestriol were found to be 0.86 ± 0.04 , 0.68 ± 0.04 , and 0.18 ± 0.02 , respectively, S & S paper No. 2043b being used. For development the paper is sprayed uniformly with a 1 per cent. soln. of phthalic

anhydride in 95 per cent. ethanol and dried at 150° C for 1 min.; it is then sprayed with a 48 per cent. soln. of ZnCl_2 in anhyd. methanol and heated at 150° C for 3 min. The yellow-green fluorescence of the oestrogens on the blue fluorescent paper is measured with a special apparatus (illustrated). Calibration curves and methods of preparing them are given. P. HAAS

801. X-ray diffraction powder data for the steroids. W. T. Beher, J. Parsons and G. D. Baker (Henry Ford Hospital, Detroit, Mich., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1569-1573.—Data for a further 39 steroids are listed and powder patterns are illustrated (cf. *Anal. Abstr.*, 1955, **2**, 2516). The steroids are classified into 16 groups. G. P. Cook

802. Spectrophotometric analysis of mixed solutes and crude organ extracts. E. Annau (Animal Diseases Res. Inst., Hull, Quebec, Canada). *Canad. J. Biochem. Physiol.*, 1955, **33** (5), 826-832.—Separation of the absorption spectra of two solutes can be achieved, when the absorption max. of the two components are well separated, by adjusting the transmittance of a reference soln. containing one of the components to 100 per cent., when only the absorption spectrum of the other component will be observed. Application of this method was illustrated with mixtures of hypoxanthine and uric acid, and hypoxanthine and xanthine. Organ extracts were prepared by ice-cold extraction of the crushed organs (brain, liver and thyroid of albino mice) with M NaCl containing $M/15$ phosphate buffer (pH 7.0) for 3 hr., followed by centrifuging for 25 min. at 0° C at 18,000 r.p.m. and diluting the soln. 1 in 10 (for brain) or 1 in 20 (for liver and thyroid). The u.v. spectra of the extracts, with 0.001 per cent. sodium ribonucleate as the reference soln., showed protein-absorption patterns characteristic of the particular organ. H. F. W. KIRKPATRICK

803. Colorimetric determination of phosphorus in phospholipids. A. E. F. H. Meijer (Leiden Univ., Holland). *Proc. Kon. Ned. Akad. Wet. B*, 1955, **58** (4), 272-281.—A critical review is given of the many colorimetric methods proposed for the determination of P, and the following procedure is recommended. *Reagents*—(a) Molybdic acid: ammonium molybdate (25 g) dissolved in about 25 ml of water to which are added 25 ml of conc. H_2SO_4 , the whole being made up to 500 ml. (b) Quinol (0.5 g) and sodium metabisulphite (15 g) dissolved in 100 ml of water; this soln. is stable for 2 weeks. (c) A standard soln. of PO_4^{3-} : KH_2PO_4 (438.9 mg) dissolved in 1 litre of water (1.0 ml \equiv 0.1 mg of P); this soln. can be preserved by the addition of a few drops of CHCl_3 . The phospholipid, containing 0.1 to 0.8 mg of P, is dissolved in 2 to 10 ml of CHCl_3 and carefully evaporated to dryness in a 100-ml Kjeldahl flask. Concentrated H_2SO_4 (0.5 ml) is added and the flask is heated over a small flame until white fumes are evolved. To accelerate oxidation a few drops of 30 per cent. H_2O_2 may be added at intervals until the soln. is colourless. Since H_2O_2 interferes with the colour reaction the heating should be continued for a few min. to remove last traces. The contents of the flask are then transferred to a calibrated 100-ml flask and 0.75 ml of 25 per cent. aq. NH_3 is added, followed by about 75 ml of water, 5 ml of reagent (a) and 2 ml of reagent (b). The contents are made up to 100 ml with water. The flask is kept in the dark

for 30 min., then the extinction is measured and compared with a calibration curve. All soln. should be kept at the same standard temp. A study of the effect of acid on the development of the blue colour showed that it reduces the extinction value, but this may be rectified by the addition of aq. NH_3 after the destruction with H_2SO_4 . P. HAAS

804. Rapid determination of serum lipids. I. Glycerol as a measure for the lipid fractions of neutral fat, lecithin and cephalin. W. Weigel (II Med. Univ. Klin. der Charité, Berlin, Germany). *Fette u. Seifen*, 1955, **57** (7), 486-490.—The lipids are extracted from a sample of serum with ethanol-ether (3:1) and saponified with NaOH solution. The soap solution is evaporated to dryness and, after acidification with H_2SO_4 , fatty acids and cholesterol are removed by filtration. The glycerol in an aliquot of the aq. filtrate is oxidised, by treatment with bromine water followed by conc. H_2SO_4 and KBr, to methylglyoxal, which is then condensed with resorcinol. The colour of the resulting orange to violet condensation product is measured in a Pulfrich photometer with filter S57. The lipid content of the serum is expressed as a range, the lower figure being based on the glycerol content of neutral fat (10.7 per cent.) and the upper figure on that of cephalin (12.3 per cent.). E. HAYES

See also Abstracts 651, 748, 754, 761.

Drugs

805. Paper chromatography in pharmaceutical analysis. III. The use of larger quantities of sample. J. Büchi and M. Soliva (Pharm. Inst., Zurich). *Pharm. Acta Helv.*, 1955, **30** (7), 265-277.—Paper chromatograms were not considered sufficient for the positive identification of a substance. In order to obtain enough of the isolated substance for chemical determination and preparation of derivatives, column chromatography is necessary. Chromatography on buffered Hyflo-Supercel (kieselguhr) was not successful for the separation of a group of antihistamines and a group of local anaesthetics, but buffered cellulose powder gave good separations and it is suggested that paper chromatography gives a good guide to the behaviour of substances on this material. In order to predict behaviour on these columns and R_F values on paper the distribution coefficients and dissociation constants were determined, the methods used being described. It was found that plotting pH against log (dissociation constant) gives a straight line for a number of antihistamines and local anaesthetics. The distribution coefficient of the undissociated form of a number of these bases is given. **IV.** J. Büchi and M. Soliva. *Ibid.*, 1955, **30** (8), 297-320.—The factors affecting R_F values on papers and the volume required for elution of columns are discussed. Methods for the determination of the paper constants are described and theoretical R_F values at various pH values are calculated from these, and the dissociation constants and distribution coefficients (cf. *Pharm. Acta Helv.*, 1955, **30**, 265) are compared with experimentally determined values. Only partial agreement is obtained, disagreement being thought to be due to changes in pH and concentration of the buffer, resulting from the movement of the solvent. It is considered as established that partition and not ion exchange is involved. Good predictions were obtained for

behaviour on buffered cellulose columns, but kieselguhr gives bad results and it is considered that paper chromatograms can be used to predict behaviour during column chromatography on cellulose. The separation of a number of anti-histamines and local anaesthetics by column chromatography is described. P. S. STROSS

806. Study of the possibility of using Cationite SDV-3 for the analysis of some pharmaceutical preparations. A. P. Arzamastsev. *Apteknoe Delo*, 1955, 4 (3), 36-39.—The resin Cationite SDV-3 is used for the determination of Ca gluconate, Ca glycerophosphate and Ca lactate. *Procedure*—A soln. containing 0.04 to 0.05 g of the salt in 10 ml of water is passed, at the rate of 2 to 3 drops per second, through a column containing 5 g of resin (previously soaked in water for 4 hr. and washed first with 3 per cent. HCl soln. and then with water until the washings are neutral to litmus). The column is washed with 30 ml of water and the free acid in the filtrate is titrated with 0.1 N NaOH. A method for determining the capacity of the resin is described. E. HAYES

807. Identification of alkaloids by paper chromatography. O.-E. Schultz and D. Strauss (Pharm.-chem. Inst., Univ. Tübingen, Germany). *Arznei-mittel-Forsch.*, 1955, 5 (6), 342-348.—The use of 14 spray reagents (in some cases combined with u.v. light) in the identification of 28 alkaloids is described, and the colours produced are tabulated. R_F values are given for the alkaloids on development with various alkaline (NH_3), neutral or acid (HCl, formic or acetic acid) H_2O -butanol systems; with the HCl- H_2O -butanol system there are two solvent fronts, and R_F values are given, which relate to the slower-moving front. Application of chemical tests enables alkaloids with very similar R_F or R_L values to be distinguished. A. R. ROGERS

808. The determination of small quantities of alkaloids with potassium iodobismuthate. W. Poethke and H. Trabert (Friedrich Schiller Univ., Jena, Germany). *Pharm. Zentralh.*, 1955, 94 (6), 219-235.—A method for the gravimetric or volumetric determination of strychnine, brucine, atropine and hyoscyamine, based on the principles developed for the determination of 8-hydroxyquinoline (cf. *Pharm. Zentralh.*, 1952, 91, 284), is described. The composition of a new compound, strychnine iodobismuthate, is given, but this varies slightly according to the conditions of precipitation. The alkaloids are determined by precipitating their iodobismuthates under exactly controlled conditions and, either determining these gravimetrically, or dissolving them in dilute HCl and titrating with KIO_3 in the presence of cyanide, starch being used as indicator. Two modifications are described, the first suitable for quantities of 1 to 30 mg, the second for quantities of 0.1 to 5 mg of the alkaloid. P. S. STROSS

809. The polarographic determination of morphine in poppy-capsules. J. Holubek (Inst. for Med. Res., Prague, Czechoslovakia). *Pharm. Zentralh.*, 1955, 94 (9), 347-349.—The morphine is converted into 2-nitrosomorphine by an excess of HNO_2 and determined polarographically. The other opium alkaloids do not interfere (cf. Baggesgaard-Rasmussen, *Bull. Féd. Int. Pharm.*, 1947, 21, 233). Good agreement with the colorimetric method (Reith and Indemans, *Brit. Abstr. C*, 1950, 371) is claimed, except for samples with very low morphine content,

when the colorimetric method is said to give erroneously low results. *Procedure*—Extract 3 g of finely powdered and dried sample with N HCl (2×100 ml) and dilute the extract to 250 ml. To an aliquot (5 ml) add N NaNO_2 (2 ml), set aside for exactly 5 min., add KOH (20 per cent.) (3 ml) and gelatin solution (0.5 per cent.) (7 drops) Pass N through the solution for 5 min. and polarograph. Determine the amount of morphine present from a calibration curve, constructed from known amounts of morphine hydrochloride. P. S. STROSS

810. The ion-exchange chromatographic separation of morphine from atropine. S. M. Blaug (Coll. Pharm., State Univ., Iowa City, U.S.A.). *Drug Standards*, 1955, 23 (4), 143-146.—Morphine sulphate (I) can be determined in the presence of atropine sulphate (II) by measuring the u.v. absorption at 285 $\text{m}\mu$; $E_{1\%}^{1\text{cm}} = 40$. I and II cannot be separated on a weakly basic resin, which converts both to the free alkaloids, but the alkaloids can be separated on a strongly basic resin which retains only the (phenolic) morphine. *Procedure*—Dilute the sample (containing 400 mg of I and 10 mg of II) to 50 ml with 75 per cent. methanol. To determine the concn. of I, dilute a 10-ml aliquot to 1000 ml with H_2O and measure the extinction at 285 $\text{m}\mu$. To determine the concn. of II, pass a 25-ml aliquot through a two-bed column containing Amberlite IR-4B (10 ml) above Amberlite IRA-410 (10 ml), elute with 75 per cent. methanol (4×10 ml) and titrate the eluate with 0.02 N HCl, with bromothymol blue as indicator. A. R. ROGERS

811. Hydroxymorphinan. VI. The paper-chromatographic estimation of morphinan derivatives and the investigation of their excretion in the dog. A. Brossi, O. Häfliger and O. Schnider (Hoffman - La Roche, Basle, Switzerland). *Arznei-mittel-Forsch.*, 1955, 5 (2), 62-66.—In the method described, buffered filter-paper is used for the separation, identification and rough estimation of a number of morphinan derivatives. Two chromatograms are run by the descending method, the first with *tert*-pentanol:di-*n*-butyl ether:water (80:7:13), the paper being buffered with phosphate buffer at pH 6.32, the second with these solvents in the ratio 50:7:43, the paper being buffered with phosphate-citrate buffer at pH 8.09. In each case the spots are stained with platonic chloride-potassium iodide solution and the unknown is compared with standards. P. S. STROSS

812. A new microchemical method for the detection of codeine and strychnine salts. V. Kwasniewski. *Pharm. Zentralh.*, 1955, 94 (1), 10-12.—The reactions of a new alkaloidal reagent, prepared by mixing red HgI_2 (0.1 g), $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 g) and water (19.8 g), are described. By mixing one drop of a solution of a codeine or strychnine salt with one drop of the above reagent characteristic crystals are obtained (two photomicrographs). Solutions of the bases themselves do not give precipitates; 48 other alkaloids (listed) and salts were examined but were found to give either only an amorphous ppt. or no ppt. P. S. STROSS

813. Alkaloidal estimation by chromatography. II. Tinctura Opii Camphorata and Tinctura Cinchonae Composita. I. Ramabhandran (Hindu Univ., Benares, India). *Indian J. Pharm.*, 1955,

17 (9), 183-185.—A column of Al_2O_3 is used for the separation of the colouring matter from the alkaloids, and a mixture of $CHCl_3$ and ethanol (2:1 for Tinct. Opii Camph. and 9:1 for Tinct. Cinchonae Co.) is used for the elution of the alkaloids. The chromatographic methods are much less time-consuming and more accurate than the official methods. O. M. WHITTON

814. **Determination of nicotine, nornicotine and total alkaloids in tobacco.** R. H. Cundiff and P. C. Markunas (R. J. Reynolds Tobacco Co., Winston-Salem, N.C., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1650-1653.—The alkaloids are removed from an alkaline tobacco mixture by extraction into benzene-chloroform soln., and aliquots are titrated with $HClO_4$ in acetic acid soln. The determination of nornicotine-type alkaloids is accomplished by acetylation of the sample with acetic anhydride before titration, and the concn. of nicotine-type alkaloids is calculated from the values of the two titrations. The standard deviation is about 0.015 per cent. over the range 2 to 5 per cent. of alkaloid, and recoveries of added nicotine and nornicotine from tobacco averaged > 98.47 per cent. Ammonia interferes but it can be eliminated in the analytical scheme. Results were in good agreement with those from other methods. G. P. COOK

815. **Studies in the genus *Digitalis*. III. The extraction and evaluation of *Digitalis purpurea* leaf.** J. M. Rowson (Pharmaceutical Soc., London). *J. Pharm. Pharmacol.*, 1955, **7** (11), 924-931.—The 3:5-dinitrobenzoic acid method (*Brit. Abstr. C*, 1953, 173) for the estimation of digitoxin or for the assay of decolorised tinctures of digitalis should be carried out with carefully standardised reagents at a controlled temperature. Tincture of digitalis prepared by 1-hr. maceration retains its potency for < 5 days. Nineteen samples of *D. purpurea* showed similar results when assayed by the 3:5-dinitrobenzoic acid method and the intravenous method with guinea-pigs. A. R. ROGERS

816. **The assay of tincture of digitalis and the determination of the constituents of *Digitalis* species.** H. Brindle, G. Rigby and S. N. Sharma (Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 942-951.—A chemical assay with 33 per cent. HCl is described for digitoxin, gitoxin and digoxin in the presence of their respective aglycones (*cf. Anal. Abstr.*, 1954, **1**, 359). Lethal-dose (for guinea-pig) and LD_{50} (for frog) values are reported for digitoxigenin and gitoxigenin and the related primary and secondary glycosides; the biological behaviour of mixtures of these constituents has also been studied. The constituents present in the Standard Preparation of Digitalis have been identified by partition chromatography on Whatman 3MM paper, with formamide as stationary phase and $CHCl_3$ as mobile phase; no aglycones were found. A. R. ROGERS

817. **Chemical and microbiological assay of penicillin V.** R. Goodey, K. N. Reed and J. Stephens (Distillers Co. Ltd., Bromborough Res. Stn., Ches., England). *J. Pharm. Pharmacol.*, 1955, **7** (10), 692-701.—An iodimetric method of assay of penicillin V (phenoxymethylpenicillin) (I), with either alkali or penicillinase as inactivating agent, is used to determine the purity of samples of I and also mixtures of I with penicillin G (benzylpenicillin). The test soln. is prepared by dissolving 100 mg of sample in 0.067 M phosphate buffer soln. (pH 7.0)

(100 ml) made up to 500 ml with H_2O . For the alkali inactivation method a blank is prepared as follows. To a 20-ml aliquot of the sample soln. are added 20 ml of 0.01 N I in 20 per cent. w/v KI soln. and the whole is titrated immediately with 0.01 N $Na_2S_2O_3$, starch being used as indicator. For the test, a 20-ml aliquot of the sample soln. is mixed with 5 ml of N NaOH and allowed to stand for 15 min. at room temperature; 5 ml of 1.1 N HCl are added, followed by 20 ml of 0.01 N I soln. After a further 15 min. the whole is titrated with 0.01 N $Na_2S_2O_3$. In the penicillinase inactivation method the test is made by the addition of 1 ml of penicillinase soln. (20 ml of water to a 30 mega-unit vial of penicillinase) to a 20-ml aliquot and the addition, after 15 min., of 30 ml of 0.01 N I soln., the whole being titrated with 0.01 N $Na_2S_2O_3$ after a further 30 min. in the dark. The difference between blank and test titrations is taken as a measure of the penicillin content, the results being quoted as "ml of 0.01 N I absorbed per mg of sample." A method for the evaluation of mixtures of I with penicillin G, based on the difference in the rates of inactivation at pH 2.0, has been developed. The greater stability of I was confirmed microbiologically. A cavity-plate method was used to compare the activity of I, in terms of penicillin G, against several recognised strains of test organisms. As the potency varies with the strain used, it is recommended that I should always be assayed against a pure sample and the results expressed on a weight basis. H. B. HEATH

818. **The assay of polymyxin and its preparations.** R. E. A. Drey, G. E. Foster and G. A. Stewart (Wellcome Chem. Wks., Dartford, Kent, England). *J. Pharm. Pharmacol.*, 1955, **7** (10), 706-715.—Details are given of the method of identification with paper partition chromatography of polymyxins A, B, C, D and E. A plate diffusion method for the microbiological assay of polymyxin B with *Brucella bronchiseptica* as the test organism is described and results show that the assay falls within the general limits of the B.P.1953. Small modifications are given for the assay of polymyxin B sulphate oily soln. and ointment of polymyxin B sulphate with bacitracin (the latter being assayed by a similar procedure with *Micrococcus flavus*). The chemical assay of polymyxin B depends on the pptn. of polypeptides as tungstophosphates and the following method is given. Transfer about 65 mg to a 50-ml beaker and dissolve in water (12 ml). Add dil. H_2SO_4 (5 ml) and 5 per cent. w/v tungstophosphoric acid in water (6 ml); allow to stand for 10 min., with intermittent stirring, and filter through a tared No. 4 sintered-glass crucible. Completely transfer the ppt. to the crucible with three 20-ml washings of 2 per cent. H_2SO_4 and wash the residue with two 20-ml and one 10-ml portion of water. Dry the ppt. at 50° C for 2 hr. (or over P_2O_5 in *vacuo* at room temp. for 4 hr.), heat at 110° C for 1.5 hr., cool and weigh. A tungstophosphate factor must be applied, based on the purest antibiotic obtainable. With modifications this method is applicable to tablets of polymyxin B sulphate and to the otic soln. Reference is made to the extension of the microbiological and chemical assay to other polymyxins, particularly polymyxin E. Some preliminary work on bacitracin is also described. H. B. HEATH

819. **The hydrolysis of aspirin in pharmaceutical preparations. A limit test for free salicylic acid.** L. J. Edwards, D. N. Gore, H. D. C. Rapson and

M. P. Taylor (Beecham Res. Lab., Betchworth, Surrey, England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 892-902.—The kinetics of hydrolysis of aspirin and the conditions for the formation and stability of the ferric-salicylate complex have been studied. A spectrophotometric method is described for the determination of free salicylic acid (I) in aspirin preparations, and results obtained with 15 preparations are compared with the B.P. limit test. *Procedure*—Suspend the powdered sample (0.2 g) in ethanol (2 ml), place in a thermostat at 25° C and add H₂O (35 ml) at 25° C; note the time. Immediately add 0.2 per cent. ferric ammonium sulphate (5 ml) and acetate-chloroacetate buffer (pH 2.95) (5 ml) and dilute to 50 ml. Shake the soln. well and, after about 10 min., filter rapidly through Whatman No. 1 paper into a 4-cm cell; note the time and measure the extinction at 530 m μ . Withdraw further samples at 10-min. intervals, measure the extinctions, and extrapolate to give the value at zero time. Calculate the concn. of I from a calibration curve. The procedure must be modified if citrates, sulphates or phosphates are present by first extracting the I into benzene.

A. R. ROGERS

820. Identification of barbiturates by paper chromatography. R. Deininger (Pharm. Inst., Univ. Munich, Germany). *Arzneimittel-Forsch.*, 1955, **5** (8), 472-475.—A method for extracting and identifying barbiturates involves chromatography on alumina and charcoal to remove impurities, and ascending paper-chromatography with an isopropyl alcohol-CHCl₃-aq. NH₃ system. The *R_F* values of 13 barbiturates are given. *Procedure*—Extract the sample (20 ml of urine or 5 ml of blood) at pH 3 with ether (50 ml). Dry the ether with Na₂SO₄ and pass it through a column of alumina (0.3 g) and active carbon (0.3 g). Wash the column with ether (2 \times 3 ml) and ether-ethanol (10:1) (3 ml), and evaporate the eluate and washings on a water bath. Dissolve the residue in methanol (0.1 ml) and apply to a strip of Schleicher and Schüll 2043b paper. If desired, confirm the presence of barbiturates by the Zwikker test (Co acetate). Develop with isopropyl alcohol-CHCl₃-25 per cent. aq. NH₃ (45:45:10) for 5 to 7 hr., dry at 60° C and determine the position of the barbiturates with HgNO₃.

A. R. ROGERS

821. Interference to the ultra-violet spectrophotometry of barbiturates. A. S. Curry (Home Office Forensic Sci. Lab., Harrogate, Yorks., England). *Nature*, 1955, **176**, 877-878.—The presence of a compound in liver which interferes with the quant. analysis of barbiturates by u.v. spectrophotometry is reported. The quantities of the compound in liver suggest barbiturate concn. of 1 to 4 mg per 100 g. In paper chromatography in a solvent system of *n*-butanol-5 *N* aq. NH₃ soln., the unknown compound runs at *R_F* 0.95, thus separating it from all the barbiturates. It also fluoresces blue in u.v. light. It does not react with the HgSO₄-diphenylcarbazone reagent for barbiturates, but gives a blue spot with FeCl₃-ferricyanide. A routine check of the ratio of extinctions at 265 m μ and 290 m μ , coupled with examination of the paper chromatogram under u.v. light, followed by elution of the fraction of *R_F* 0.95 with 0.1 *N* NaOH, in which its spectrum is the same as in 0.5 *N* aq. NH₃ soln., as distinct from the barbiturates, will show its presence. If present, the compound must be separated from an aliquot of the extract on a paper chromatogram

before the barbiturate is quant. analysed by u.v. spectrophotometry. In one instance, this compound was isolated from the liver and a compound having similar u.v. light absorption characteristics was isolated from the contents of the stomach, suggesting that the substances may be metabolically related.

O. M. WHITTON

822. The volumetric determination of Veramon and similar preparations. W. Poethke and D. Horn (Friedrich Schiller Univ., Jena, Germany). *Pharm. Zentralh.*, 1955, **94** (2), 41-45.—The determination of mixtures of barbitone and amidopyrine or of similar mixtures is described; no preliminary separation is necessary. *Barbitone*—Dissolve material equivalent to 1 millimole of barbitone in CO₂-free ethanol (24 ml), add 0.1 per cent. ethanolic thymolphthalein solution (1 ml) and CO₂-free water (15 ml). Titrate the solution with carbonate-free 0.1 *N* NaOH till the colour matches that of a standard consisting of CuSO₄·5H₂O (7.85 mg) and K₂Cr₂O₇ (0.285 mg) dissolved in dilute aq. NH₃ (50 ml). Subtract 0.03 ml from the titre obtained. *Amidopyrine*—Dissolve material equivalent to 0.1 g of amidopyrine in chloroform (10 ml), add 0.05 per cent. dimethylaminoazobenzene in chloroform (5 drops) and titrate with 0.05 *N* toluene-*p*-sulphonic acid in chloroform (1 ml \equiv 11.56 mg of amidopyrine). Alternatively, 0.03 *N* HCl in chloroform can be used. The acid solutions are standardised against hexamethylenetetramine, with 1 per cent. phenol in chloroform as solvent. P. S. STROSS

823. Lignocaine hydrochloride and its solutions: purity, tests, stability and assay. K. Bullock and J. Grundy (Univ. Manchester, England). *J. Pharm. Pharmacol.*, 1955, **7** (10), 755-773.—Samples of lignocaine and its anhydrous and monohydrated hydrochlorides were synthesised and purified by recrystallisation. With these as analytical standards a number of assay processes have been examined, the most convenient method being the titration of the excess of acid added to the base with standard alkali, bromocresol green being used as indicator. To determine the percentage decomposition of soln. of lignocaine, a colorimetric method has been devised, based on the reaction of the decomposition product, 2-amino-1:3-dimethylbenzene, with 4-aminophenazone and K₃Fe(CN)₆. By this method less than 0.1 per cent. of decomposition in a 2 per cent. soln. of the hydrochloride can be detected.

H. B. HEATH

824. Determination of leptazol. S. Bhattacharya, S. C. Banerjee and B. C. Dutta (Bengal Immun. Res. Inst., Calcutta, India). *Indian J. Pharm.*, 1955, **17** (6), 114-115.—The effect of temperature on the assay of leptazol prescribed in the B.P. 1953 has been investigated and results show that values for leptazol become lower as the reaction temp. increases beyond 15° C. It is recommended that pptn. should be carried out at a temp. not exceeding 15° C.

H. B. HEATH

825. The spectrophotometric assay of an anti-histamine combination. S. M. Blaug and L. C. Zopf (Coll. of Pharm., State Univ. of Iowa, Iowa City, Iowa, U.S.A.). *Drug Standards*, 1955, **243** (4), 147-148.—A solution of two antihistamines can be assayed for both constituents by determining the u.v. absorption at two wavelengths and allowing for the contribution of each constituent at each wavelength. The method is demonstrated by

reference to the analysis of a mixture of pyrobutamine diphosphate and methapyrilene hydrochloride.

A. R. ROGERS

826. The separation and volumetric determinations of aluminium, bismuth, calcium and magnesium, in pharmaceutical preparations. H. E. Brookes and C. A. Johnson (Boots Pure Drug Co., Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 836-850.—Published methods for the volumetric determination of Al and of Bi with EDTA (disodium salt) have been examined, and methods are given for the determination of Al, Bi, Ca and Mg in the presence of each other. These methods are applied to the analysis of pharmaceutical products, including the assay of Compound Lozenges of Bismuth B.P.C. for Bi, Ca and Mg. The results compare favourably with those obtained by classical methods. *Determination of Al*—To the sample (containing 15 to 20 mg of Al⁺⁺⁺) add 0.1 N EDTA (disodium salt) (25 ml) and H₂O (80 ml). Neutralise with aq. NaOH to Congo red, add 2 M chloroacetic acid (5 ml), M Na acetate (10 ml) and 0.1 per cent. aq. alizarin red S (1.5 ml) and titrate with 0.1 N thorium nitrate to a blue-red end-point. *Determination of Bi*—Dilute the sample (\approx 120 mg of Bi⁺⁺⁺ in dil. HNO₃) to 50 ml with H₂O, add 0.1 per cent. aq. catechol violet (2 drops) and aq. NH₃ until the soln. is deep blue. Titrate with 0.1 N EDTA (disodium salt) to a bright-yellow end-point, diluting the soln. with H₂O (200 ml) and adding more indicator during the titration. Oxidising agents must be absent. Bismuth and Al may be determined together by the thorium nitrate method; Bi and Mg, or Bi and Ca, may be determined together by the usual Solochrome-black method in ammoniacal soln. Bismuth may be removed before the determination of Mg and Ca by pptn. as the oxycarbonate; Al in the presence of Mg and Ca may be masked by complexing with triethanolamine.

A. R. ROGERS

827. The spectrophotometric assay of injection solutions containing chlorocresol. L. Brealey and K. A. Proctor (Boots Pure Drug Co., Ltd., Nottingham, England). *J. Pharm. Pharmacol.*, 1955, **7** (11), 830-835.—Spectrophotometric methods have been used to assay injection solutions containing chlorocresol (I) as bactericide. When the absorption of the active ingredient (*e.g.*, procaine) is much higher than that of I, then I can be ignored. When the absorption curves are different, and the absorption of the active principle (*e.g.*, pethidine, methylamphetamine) is not less than that of I, measurements can be made at the two absorption maxima. Preliminary separation is necessary when the absorption curves of the active principle (*e.g.*, atropine, strychnine, apomorphine, morphine) and I are similar, or when the absorption of the active ingredient is less than that of I. Partition chromatography on kieselguhr buffered at pH 11.4, with cyclohexane as mobile phase, is a suitable method of separation with apomorphine or morphine.

A. R. ROGERS

828. Content of copper in galenicals. I. The dithiocarbamate method and its applicability. S. A. Schou (Rigshospitalets Apotek, Copenhagen, Denmark). *Dansk Tidsskr. Farm.*, 1955, **29** (9), 202-213.—Current techniques for the application of the dithiocarbamate method (*cf.* Schou, *Arch. Pharm. Chem.*, 1954, **61**, 524; Jewsbury, *Brit. Abstr.*

C., 1953, 417; and Jenkins, *Anal. Abstr.*, 1954, **1**, 1768) to the determination of Cu in crude drugs and galenicals are described. A standard graph is given for the spectrophotometric determination of the Cu complex at 436 m μ . Solutions of the Cu complex in carbon tetrachloride are sufficiently stable, when kept during 6 weeks in sealed vessels in the dark, to be useful in preliminary determinations.

P. S. ARUP

829. Volumetric determination of water by the Karl Fischer titration. II. Determination of water in medicinal tars. V. G. Jensen (Danish Pharm. Coll., Copenhagen, Denmark). *Dansk Tidsskr. Farm.*, 1955, **29** (10), 225-237.—Water can be determined in the tars by the Karl Fischer method, with the electrometric "dead-stop" technique, provided that a volume (usually 20 ml) of anhyd. chloroform equal to that of the pyridine-SO₂ reagent is added to the reagent to keep the tar in soln. In the absence of water, side-reactions are shown to occur between the tar (especially juniper tar) and excessive amounts of the titrating reagent, but a constant galvanometer end-point deflection lasting for 10 to 20 sec. (according to the nature of the tar) can be expected, provided that the titration is carried direct to the end-point, with additions during the final stages not exceeding 0.05 to 0.1 ml of the titrating reagent. Johansson's modification of the Karl Fischer method (*Pharm. Dan.*, 48, Addendum) can be used similarly with equal success.

P. S. ARUP

830. Purity tests. IX. Limit test for turbidity [of solutions of drugs]. K. Ilver, Aa. Jackerott and F. Reimers. *Dansk Tidsskr. Farm.*, 1955, **29** (7), 153-171.—Various methods for the preparation of reproducible nephelometric standards, suitable for the assessment of the clarity of solutions of drugs, are critically examined, and the following method is recommended. *Procedure*—To 1 ml of ethanolic (85 per cent. w/w) BaCl₂ containing 0.5 mg of Ba, is added 1 ml of M H₂SO₄ from a pipette while the mixture is shaken. After being set aside for 5 min., the mixture is diluted with water to 10 (or to 50) ml. This standard remains constant during 20 min., and is used for direct visual comparison in daylight against a black background.

P. S. ARUP

831. The determination, in forensic medicine, of habit-forming drugs by paper chromatography. E. Vidic (Inst. für gericht. soziale Med. der Freien Univ., Berlin, Germany). *Arzneimittel-Forsch.*, 1955, **5** (5), 291-295.—Examination of a large number of urine specimens from addicts has shown that paper chromatography with the solvent system butanol-formic acid-H₂O (12:1:7) is not sufficient to separate and identify habit-forming drugs. The *R_F* values are unreliable, and other organic bases interfere. The system dichloroethane-acetic acid-H₂O (10:4:1) should also be used; a table of *R_F* values is given. In forensic medicine, the results by paper chromatography should be confirmed by chemical methods, and the principal tests are cited.

A. R. ROGERS

832. Toxicological determination of carbon disulphide. R. Ertola. *Monit. Farm.*, 1955, **61**, 325-329.—The iodimetric titration is satisfactory for quantities > 100 μ g. Interfering substances (H₂S, SO₂, HCN) are removed by 10 per cent. KOH.

To a weighed amount, 1 or 2 ml of alcoholic KOH are added, then acetic acid till the solution is acid to phenolphthalein but alkaline to litmus, followed by 0.05 g of NaHCO_3 and 1 ml of starch solution. This solution is immediately titrated with I to a stable, faint blue. Amounts between 10 and 800 μg , but > 0.2 mg, per ml, are best estimated colorimetrically with a solution of 0.05 g of Cu acetate, 1 ml of diethylamine and 20 ml of triethanolamine, made up to 1 litre with 95 per cent. ethanol. In the latter method H_2S must be removed by lead acetate paper. In fresh viscera 80 per cent. of the CS_2 in the vacuum distillate is determinable but, after putrefaction, treatment with N NaOH is necessary and only 65 to 70 per cent. is then determinable.

T. R. MANLEY

See also Abstracts 761, 785, 786, 850, 851.

Food

833. Accurate determination of arsenic in foods and feeding-stuffs. W. Deckert. *Chem. Tech., Berlin*, 1955, 7 (8), 480-483.—A modified form of the Marsh method is described for estimating the arsenic content in foodstuffs and animal feeding-stuffs. The Marsh arsenic mirrors are estimated by titration, and steps are taken to ensure that all As present is deposited as a mirror. The decomposition of the As-containing sample with Zn and H_2SO_4 is effected by an acid mixture which avoids violent liberation of hydrogen. To ensure that all the As is collected as mirror, a lengthened capillary is used and a second heated zone is added. The mirrors are dissolved in a solution of ICl containing CCl_4 and the iodine liberated by reaction between the As and ICl is titrated with 0.025 M (or 0.0025 or 0.00025 M) KIO_3 from a micro-burette until the iodine coloration of the CCl_4 disappears. (1 ml of 0.00025 M $\text{KIO}_3 \equiv 0.15$ mg of As.) Comparative determinations of standard solutions of As and of As-containing feeding-stuffs by the new and older methods show that the new method gives higher results which are much nearer the true values. The method is capable of detecting 0.00015 mg of arsenic.

H. L. WHITEHEAD

834. A sensitive method for measuring lipase activity and its application to wheat products. W. W. Luchsinger, L. S. Cuendet, P. D. Boyer and W. F. Geddes (Univ. of Minnesota, St. Paul, Minn., U.S.A.). *Cereal Chem.*, 1955, 32 (5), 395-404.—A colorimetric method is described for measuring low levels of lipase activity. The method is based on the hydrolysis of a mono-olein emulsion at pH 7.4, at 30°C , and subsequent estimation of the glycerol released by cleavage with periodate and treatment of the resulting formaldehyde with chromotropic acid. From 0.2 to 18.0 μg of glycerol can be determined. In applying the method to wheat products, homogenates of the residue remaining after successive extractions with light petroleum and $(\text{NH}_4)_2\text{SO}_4$ soln. (95 per cent. saturated) are used as the enzyme sources. The results agree fairly well with those obtained by other methods.

S. C. JOLLY

835. Determination of some components in corn syrups by quantitative paper-chromatography. R. L. Whistler and J. L. Hickson (Purdue Univ. Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1955, 27 (10), 1514-1517.—A method for the determination of nine corn-syrup components, tentatively identified as

glucose, maltose, isomaltose, maltotriose, isomaltotriose, maltotetraose, maltopentaose, maltohexaose and maltoheptaose, is described. These components are separated chromatographically by the descending technique, with filter-paper and a mixture of *n*-butanol, ethanol and water (2:1:1) as the principal solvent. The components are quant. determined by the anthrone- H_2SO_4 , 1-naphthol- H_2SO_4 , phenol- H_2SO_4 and the alkaline 3:5-dinitrosalicylic acid-phenol absorptiometric techniques. The R_F values decrease from glucose to maltoheptaose in the order shown above. The method was applied to the analysis of eight corn syrups of various degrees of hydrolysis and gave mean deviations of $< \pm 1.3$ per cent. for each component.

G. P. COOK

836. Detection and determination of hydroxymethylfurfuraldehyde in genuine and artificial honey.

O. Winkler (Inst. Pharm. Chemie, Universität Marburg a.d. Lahn, Germany). *Z. Lebensmitt.-Untersuch.*, 1955, 102 (3), 161-167.—*Spectrophotometric method*—This method is based on the observation that whilst the spectrophotometric extinction values (E) of soln. of genuine honey increase linearly over the range 325 to 245 $m\mu$, the values for aq. soln. of hydroxymethylfurfuraldehyde (I) rise steeply to a max. at 282 $m\mu$, and are negligible at 325 and 245 $m\mu$. Any significant deviation of E at 285 $m\mu$ from the mean of the values at 325 and 245 $m\mu$ can thus be used as a measure of the content of I. *Procedure A*—Ten ml of a 20 per cent. (w/v) soln. of the sample are diluted with 50 ml of water, mixed with 1 ml each of aq. 15 per cent. $\text{K}_4\text{Fe}(\text{CN})_6$ soln. and 30 per cent. Zn acetate soln., made up to 100 ml and filtered. The clear filtrate is used for the measurements of E (E_{325} , E_{285} and E_{245}). When a 1-cm cell is used, the content of I (mg per 100 g) is given by the formula— $43.1 [E_{285} - 0.5 (E_{245} + E_{325})]$. *Photometric method*—This method is based on the colour reaction given by I with a mixture of *p*-toluidine and barbituric acid, and can be carried out semi-quantitatively by visual comparison, or quantitatively with a simple photometer or a step-photometer with filter S55. *Procedure B*—For the semi-quantitative estimation, two 2-ml portions of a 20 per cent. (w/v) soln. of the sample are mixed with 5 ml of a 10 per cent. soln. of *p*-toluidine in isopropanol containing 10 per cent. of acetic acid. To one portion is added 1 ml of aq. 0.5 per cent. barbituric acid and, to the other, 0.7 ml of water and 0.3 ml of a 0.01 per cent. soln. of neutral red, which has been slightly acidified with acetic acid; the colorations are compared 3 min. after mixing; the neutral-red coloration is equivalent to 5 mg of I per 100 g of the sample. *Procedure C*—Two soln. are prepared as described above, with the exception that 1 ml of water is substituted in the second soln. for the water and neutral-red soln.; this second soln. is used as a blank. When a 1-cm cell is used, the content of I (mg per 100 g) is equivalent to $19.2 E$, E being the extinction value at 550 $m\mu$, determined 3 to 4 min. after mixing. Both methods show reasonable accuracy and mutual agreement. Genuine honey (11 samples) contained 0 to 4 mg, and artificial honey (3 samples) 50 to 150 mg of I per 100 g of the sample.

P. S. ARUP

837. Chromatography of sugars on paper. I. Results with the system ethyl acetate-pyridine-water. J. Moreno Calvo. *An. Bromatol.*, 1955, 7 (2),

95-105.—A piece of Whatman No. 1 filter-paper (40 cm × 41 cm) is sewn together along the 40-cm edges, after the paper has been spotted with the liquids under examination (1-6 μ l of a 1 per cent. soln. is a suitable amount). The paper cylinder so obtained is then stood vertically, spots at the lower edge, in a Petri dish containing the solvent (2 pt. of ethyl acetate, 1 pt. of pyridine and 2 pt. of water, the non-aqueous liquid after agitation and separation being used). The liquid rises toward the upper edge of the paper and, after 24 hr., the chromatogram is developed with a reagent comprising 930 mg of aniline and 1.6 g of phthalic acid in 10 ml of water saturated with butanol. The R_F values for arabinose, glucose, mannose, fructose, sucrose, lactose and raffinose are recorded, and it is shown that the length of the spot after elution = $f \log C + b$, where f and b are constants and C is the concn.

II. Application to foodstuffs and other natural substances. J. Moreno Calvo. *Ibid.*, 1955, 7 (2), 107-115.—With the technique described in Part I, and acid aniline phthalate or 0.2 per cent. ninhydrin in butanol-methanol (95:5), the eight hexoses named can be separated in a solution containing 1 per cent. of each. Coffee, milk saturated with boric acid, sherry, orange juice, beer and apricots have been tested by this method.

L. G. L. UNSTEAD-JOSS

838. "Albuminoid ammonia" value in analysis of jam. S. N. Mitra. *J. Inst. Chem., India*, 1955, 27 (1), 31-36.—The sample is freed from stones and homogenised, and 5 g are digested with 100 ml of water on a bath of boiling water for 1 hr., and frequently stirred. The soln. is filtered through muslin into a 250-ml flask, cooled and made up to vol.; 50 ml are withdrawn, neutralised with 0.1 N NaOH, diluted to 250 ml and distilled. The first 100 ml of distillate are discarded and 50 ml of alkaline $KMnO_4$ reagent with 6 g of solid $KMnO_4$ are then added to the liquid left in the distillation flask and distilled. A suitable aliquot of distillate is diluted to 50 ml, 2 ml of Nessler reagent are added and the colour produced after 5 min. is matched with that produced by aliquots of standard NH_4Cl , similarly treated. The method is useful in checking the approx. fruit content of jam.

S.C.I. ABSTR.

839. Application of circular paper chromatography method for the detection of adulteration in milk. B. V. Ramachandra, N. N. Dastur and K. V. Giri (Indian Dairy Research Institute, Bangalore, India). *Indian J. Dairy Sci.*, 1955, 8 (2), 83-88.—Milk adulterated with water with the addition of sufficient sucrose to make it isotonic with milk may be detected by a chromatographic technique; as little as 5 per cent. of water (with the necessary sucrose) is detectable. The milk under examination is diluted ten-fold and 20 μ l are spotted on to filter-paper. The solvent used is *n*-butanol-pyridine-water (6:4:3), and irrigation with the solvent is carried out twice. Colour is developed by applying a mixture of equal volumes of 2 per cent. triphenyl-tetrazolium chloride and N KOH in 95 per cent. ethanol; the temp. of the paper is then raised from 45° to 80° C in 20 min. and held at 80° C for 20 min. in an atmosphere as nearly saturated with moisture as possible. The presence of sucrose is clearly indicated by a coloured band at a radius larger than that of lactose.

L. G. L. UNSTEAD-JOSS

840. A simple method for the determination of the degree to which milk has been neutralised. K. Woidich and L. Schmid (Chem. Univ. Lab., Vienna). *Z. Lebensmittelforsch.*, 1955, 102 (3), 167-171.—The authors have established by numerous analyses that normal mixed milk (occurring in practice in bulks of > 12 gall.) requires, irrespective of its initial pH or acidity, a constant proportion of standard acid for the reduction of its pH value to 2.7. Any excess over this constant potentiometric titre, viz, 10.1 ± 0.1 ml of 0.25 N HCl per 25 ml of milk, indicates the previous addition of alkali to the milk. The presence in 25 ml of milk of alkalinity derived from 0.0084 g of $NaHCO_3$ can be detected by an excess in the titre of 0.4 ml. The titre of individual milks may vary from 9.1 to 12.3, but that of a mixture of two such milks, even if the titre of each is abnormally high or abnormally low, approximates to 10.1. Neither pasteurisation nor the presence of formaldehyde interferes with the test. *Procedure*—The titration is carried out on 50 ml of milk with standard potentiometric apparatus; the first 18 ml of 0.25 N HCl are run in, with efficient stirring, during 30 sec., after which the acid is added dropwise. The results are expressed in terms of 0.25 N HCl per 25 ml of milk.

P. S. ARUP

841. A bacterial enzymatic method for determining tyrosine in cheese. G. J. Silverman and F. V. Kosikowski (Cornell Univ., Ithaca, N.Y., U.S.A.). *J. Dairy Sci.*, 1955, 38 (9), 941-949.—The method described, which is specific for free tyrosine (I) in ripened Cheddar cheese, is based on the decarboxylation of I in an aq. suspension of the sample by an active decarboxylase preparation obtained from *Streptococcus faecalis*, Strain R. The resulting tyramine (II) is extracted with five portions of ether from the aq. soln. adjusted to pH 10.5 and then determined colorimetrically with Millon's reagent or, less satisfactorily, with Folin-Ciocalteu reagent. Free II present in the sample is determined on a separate portion, the decarboxylase treatment being omitted. Formulae are given for calculating free I, total I liberated from the protein during ripening and free II in the sample. An apparatus for the simultaneous extraction of 10 samples is described.

W. H. C. SHAW

842. The detection of triacetin by paper chromatography. G. Cerutti and A. Tamborini (Univ. Milan, Italy). *Ann. Sper. Agr.*, 1955, 8, 1723-1726.—Triacetin (I) in adulterated butter can be detected by paper chromatography. A chromatogram of the water-soluble acids is obtained from the aq. soln. resulting from Reichert-Meissl treatment. By using as solvent a mixture (1:1) of 95 per cent. ethanol and isobutyl alcohol, containing 1 per cent. of conc. aq. NH_3 , and developing with 0.05 per cent. bromophenol blue at 50° C, distinctive spots for the volatile acids and for I are obtained. The R_F of I is 0.24; 0.5 per cent. of I may be detected.

H. A. FISHER

843. Contributions to colour and turbidity measurement in wort and beer with a new small Zeiss electrophotometer. H. Hecht. *Brauwissenschaft*, 1955, (8), 175-178.—The new Zeiss electrophotometer, Elko II, described and illustrated, is used to eliminate errors associated with personal observation of colour in beer and wort. S.C.I. ABSTR.

844. Comparative studies of methods of hop analysis. I. Estimation of moisture content.

L. R. Bishop (Stag Brewery, Pimlico, London, England). *J. Inst. Brew.*, 1955, **61** (5), 386-393.—The results of a series of investigations carried out in 14 countries, and promoted by the Analysis Committee of the European Brewery Convention, are reported. A major source of error is the rapid gain or loss of moisture by hops exposed to air of varying humidity, which necessitates strict precautions in sampling, transport of samples, and analytical procedure to avoid no more than momentary exposure to the atmosphere. As a reference method, drying over P_2O_5 in a vacuum-desiccator for four weeks is proposed. Distillation entrainment in a Dean and Stark apparatus with methylcyclohexane or *n*-heptane (10 g of hops with 150 ml of solvent in a 250-ml flask) gave satisfactory results. Routine oven-methods, using flat aluminium dishes with lids (7 to 10 cm diam. and 2 to 3 cm deep), with 3 to 5 g of hops, dried for 1 hr. at 106° C, or 1.5 hr. at 98° C, are also satisfactory. The Fischer method tends to give low results.

S.C.I. ABSTR.

845. Turbidimetric method for the determination of yeast mannan and glycogen.

J. A. Cifonelli and F. Smith (Univ. Minn., St. Paul, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1639-1641.—The globulin, concanavalin-A, which is extracted from jack-bean meal, was utilised to determine yeast mannan and glycogen. The globulin interacts with these polysaccharides to give a ppt., which is measured turbidimetrically. Suitable concentration ranges are 10 to 100 μ g per ml for yeast mannan and 100 to 1000 μ g per ml for the glycogen.

G. P. COOK

846. The flame-photometric determination of and the content of potassium and sodium in wine.

J. Wurziger (Staatlichen Chem. Untersuchungsanstalt, Bremen, Germany). *Dtsch. LebensmittlRdsch.*, 1955, **51** (5), 124-130.—The rapid estimation of Na and K in wine is possible by flame photometry of a 1:10 dilution in water. The significance of the content of Na and K, expressed as a percentage of the ash, of wines from 155 different sources is discussed.

A. R. ROGERS

847. The determination of citric acid as pentabromoacetone and its application to wines. I. Gravimetric method.

O. Reichard (Dillingen, Bavaria, Germany). *Dtsch. LebensmittlRdsch.*, 1955, **51** (9), 218-224.—The conversion of citric acid into pentabromoacetone (I) is interfered with by the presence of sugar, colouring and tanning agents, etc. Quantitative separation is achieved as Ba citrate, which is insol. in 70 per cent. ethanol. The Ba citrate formed is separated by centrifuging, and treated with 5 to 10 per cent. H_2SO_4 to obtain citric acid soln., after filtering off $BaSO_4$. The use of ion-exchange resins offers no advantage over the above procedure. Determinations of citric acid as I, in various media, are described, but the following general procedure is given. Neutralise 25 ml of wine in a glazed porcelain or platinum dish, add 5 ml of 10 per cent. $BaCl_2$ soln. and evaporate on a water bath to \approx 5 ml. While still hot wash the residue into a 50-ml graduated centrifuge tube with 5 ml of hot H_2O , mix with 5 vol. of 96 per cent. ethanol and centrifuge. Wash the residue twice with 70 per cent. ethanol, drain well and gradually mix well with 20 ml of 10 per cent. H_2SO_4 . Add 2.5 ml of a soln. containing 10 g of KBr and 2.3 g

of $KBrO_3$ in 100 ml of H_2O , make up to 25 ml with H_2SO_4 and centrifuge. Place 20 ml of clear liquid into a 50-ml beaker and cool to 0° C; add, dropwise, 5 per cent. $KMnO_4$, each new addition being made when the purple colour has disappeared, until a brown turbidity and precipitate persist for 30 min. at 0° C. Add sulphurous acid, dropwise, to remove the dark colour and, if necessary, $KBr-KBrO_3$ soln. Collect the ppt. on a sintered-glass funnel, wash twice with cold water, dry to constant weight over P_2O_5 or conc. H_2SO_4 , and weigh. Tare the glass filter alone after the weighing, as glass is attacked slightly during the analysis. The method gives results 92 to 94 per cent. of theoretical, and reliable results are claimed by adjusting the factor from 0.4642 to 0.5. The preparation of pure I is described; it has been microscopically, physically and chemically characterised.

H. A. FISHER

848. Determination of the setting-point of fats and similar substances with a rotating thermometer.

F. Neuwald and K. Adams. *Arch. Pharm., Berlin*, 1955, **288** (6), 280-284.—A method is described, which is reproducible to $\pm 1^\circ C$, for the determination of the setting-point of fatty materials, e.g., lanolin, paraffin wax, soft paraffin, etc. A 0° to 100° C mercury thermometer with 0.5° graduations, the bulb of which has been previously warmed, is coated with the molten fatty material which has been gently heated 5° to 10° C above its setting-point. The lower portion of the thermometer stem is quickly enclosed in a glass insulating sleeve warmed to the same temp. and closed at one end, with a bored cork at the other for the thermometer. The thermometer is held in a horizontal position and slowly rotated (once in 2 sec.) until the drop suspended from the bulb rotates with the thermometer. This is taken as the setting-point.

G. R. WHALLEY

849. Paper chromatography in the fat field.

XVII. Separation of unsaturated fatty acids. H. P. Kaufmann and W. H. Nitsch. *Fette u. Seifen*, 1955, **57** (7), 473-474.—The methods previously described for the separation of saturated fatty acids (*cf. Anal. Abstr.*, 1955, **2**, 2557) are applied to unsaturated acids. Oleic and linoleic acids can be separated on paper impregnated with paraffin (boiling range 190° to 220° C) with a mobile phase of 90 per cent. acetic acid saturated with the same paraffin. The 9:11- and 9:12-linoleic acids could not be separated under the same conditions; the R_F values of *cis-trans* isomers, such as oleic and elaidic acids, are also too close to permit efficient separation.

E. HAYES

850. The spectrophotometric determination of vitamin D in pharmaceutical preparations. II.

Tablets of Calciferol B.P. A. R. Rogers (Allen and Hanburys, Ltd., Ware, Herts., England). *J. Pharm. Pharmacol.*, 1955, **7** (10), 731-737.—The conditions for the extraction and determination of vitamin D from tablets are investigated and two alternative methods of assay are recommended. In the first method the tablets are extracted with 1:2-dichloroethane, and the colour produced with a soln. of $SbCl_5$ in 1:2-dichloroethane is measured at 550 m μ . In the second method the vitamin is eluted from a chromatographic column and determined as before. The results indicate that the methods are accurate for fresh tablets and give a good estimate of the potency of partly decomposed tablets.

H. B. HEATH

851. The chemical estimation of calciferol in pharmaceutical preparations. P. S. Stross and L. Brealey (B.D.H. Ltd., Graham St., London). *J. Pharm. Pharmacol.*, 1955, **7** (10), 739-750.—The assay of calciferol in a number of preparations is thoroughly investigated with direct spectrophotometric and infra-red methods, and SbCl_3 -acetyl chloride reagent. Although the absorption curves of the calciferol-containing fraction obtained after chromatography are generally identical with those of pure calciferol, a three-point correction is sometimes necessary, particularly when a high proportion of the original calciferol has been decomposed (60 per cent. or more). In the analysis of oils having comparatively low calciferol content, saponification followed by chromatography of the unsaponifiable matter does not remove all substances that interfere with the spectrophotometric assay, and hence high results are obtained. Decomposition products appear to give practically no colour with SbCl_3 -acetyl chloride reagent and a chromatographic step is unnecessary in the assay of tablets of calciferol. For low-potency oily soln. of calciferol, chromatography is necessary to remove phytoosterols. Methods are given for the assay of the B.P. Solution and Tablets of Calciferol; results obtained are in good agreement with those obtained by biological assay.

H. B. HEATH

852. Polarographic determination of the riboflavin and thiamine contents of foods. E. Kevei, M. Kiszal and M. Simek (Inst. Res. in Canning, Meat Packing and Refrig., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1955, **6** (3-4), 345-363.—Riboflavin is extracted in 0.1 N HCl and any bound vitamin is liberated with taka-diastase. For purification, the riboflavin is adsorbed on fuller's earth activated with KCl, and eluted with hot 80 per cent. acetone. The extract is clarified with basic Pb acetate. The determination is carried out in a phosphate buffer of pH 7.6, E_1 being -0.57 V (measured against a S.C.E.). Thiamine is extracted in an alcoholic HCl soln., and any bound vitamin is liberated with taka-diastase. For purification, the thiamine is adsorbed on charcoal activated by steam and KCl, and eluted with 0.2 N HCl followed by 25 per cent. ethanol. Although the adsorption is quant., only 90 per cent. of the vitamin may be eluted, so that a correction factor for each batch of adsorbent must be evaluated. The determination is carried out in an acetate buffer of pH 6.2, E_1 being -1.34 V (measured against a S.C.E.). The difference between parallel determinations of standard riboflavin and thiamine soln. are > 2.5 and 5 per cent., respectively.

J. H. WATON

853. The determination of ascorbic acid with tetrazolium salts. Z. Padre, M. Smid and V. Sicho (Forschungsinstitut Pharm. und Biochemie, Technische Hochschule, Prague). *Naturwissenschaften*, 1955, **42** (8), 210-211.—The mixture to be analysed is run in *n*-butanol, acetic acid and water (4:1:5) in an atmosphere of N to produce circular chromatograms. Ascorbic acid becomes immediately visible at room temperature on being sprayed with alkaline tetrazolium salts, whereas reducing sugars do not react until the paper is heated in the drying cabinet. The method is sensitive to $15 \mu\text{g}$ of ascorbic acid. For quantitative work elution of the spots is recommended (no working details are given).

E. KAWERAU

854. Identification of stored-products insects by the micromorphology of the exoskeleton. I. Elytral patterns. R. F. Heuermann and O. L. Kurtz (Food and Drug Admin., Minneapolis, Minn., U.S.A.). *J. Ass. Off. Agric. Chem.*, 1955, **38** (3), 766-781.—Reproductions of the micro-structure of the hardened outer wing-covers of 20 beetles and weevils are accompanied by a classification key and descriptions by species.

A. A. ELDRIDGE

See also Abstract 651.

Sanitation

855. Use of EDTA for determining iron in natural waters. A. A. Bashkirtseva and E. M. Yakimets (S. M. Kirov Univ. Polytech. Inst.). *Zavod. Lab.*, 1955, **21** (5), 533-535.—Three 100-ml portions of the water are taken. The acidity or alkalinity is determined in the first sample and the other two are neutralised accordingly with 0.1 N acid or alkali. To these are added 4 ml of $\text{N H}_2\text{SO}_4$ and the Fe is oxidised in the boiling solution by addition of KMnO_4 or $\text{K}_2\text{S}_2\text{O}_8$. With contents of Fe > 1 mg per litre the solution is cooled to 50°C and with lower contents to 60°C . Five ml of 40 per cent. NH_4SCN solution are added and the solution is titrated with 0.1 N EDTA (disodium salt) until the red colour of $\text{Fe}(\text{SCN})_3$ disappears; towards the end of the titration the titrant is added slowly, in drops. With large amounts of Fe the end-point is difficult to see. One portion is therefore over-titrated and is used as a reference for the titration of the second.

G. S. SMITH

856. Flame-photometric determination of chloride in sea water. M. Honma (U.S. Naval Radiological Defence Lab., San Francisco, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1656-1659.—By modifying the Beilstein test, concn. from 0.02 to 0.5 M of chlorides in sea water can be determined by flame photometry with an accuracy equiv. to that of the Mohr titration. Ten ml of soln. containing 2.5 ml of sample plus 5 ml of 1.26 M $\text{Cu}(\text{NO}_3)_2$ are aspirated into the oxy-hydrogen flame and the intensity of the CuCl band (D system) is measured at $437 \text{ m}\mu$ and a slit-width of 0.34 mm. A calibration curve for NaCl is prepared from data for synthetic sea water and $\text{Cu}(\text{NO}_3)_2$ soln. The sensitivity is not good mainly because very small changes in hydrogen pressure (≈ 1 in. of H_2O) affect the emission of CuCl.

W. J. BAKER

857. Colorimetric determination of traces of boron [in natural water, with carmine red]. Hiroshi Kawaguchi (Nagoya Univ., Chigusa-ku, Nagoya, Japan). *Japan Analyst*, 1955, **4** (5), 307-310.—Experimental conditions for the colorimetric determination of boron with carmine red in a conc. H_2SO_4 soln. (Hatcher and Wilcox, *Brit. Abstr. C*, 1950, 437) were studied from the aspect of its application to the analysis of natural water (containing 0.1 to 10 mg of B per litre). The sample is evaporated to dryness in an alkaline soln. and distilled in the presence of methanol from an HCl soln. The distillate is evaporated to dryness, and treated with carmine red in H_2SO_4 . The extinction at $610 \text{ m}\mu$ is proportional to the amount of B for amounts $< 20 \mu\text{g}$ per 2 ml. Fluoride and nitrate interfere with the colour, but both are separated from B by the distillation.

K. SAITO

858. Determination of free formaldehyde [in water]. D. K. Owens (N. Carolina State College, Raleigh, N.C., U.S.A.). *Sewage Ind. Wastes*, 1955, **27** (8), 939-940.—A method for determining formaldehyde (I) in turbid or highly coloured waters consists in adding to 2 ml of 1 per cent. aq. phenylhydrazine hydrochloride, in a separating funnel, 8 ml of sample (> 0.7 p.p.m. of I), setting aside for exactly 10 min., adding 1 ml of fresh 5 per cent. aq. $K_3Fe(CN)_6$, setting aside for exactly 5 min., adding 4 ml of conc. HCl followed by 15 ml of *n*-butanol, and shaking vigorously. The alcohol layer is separated (and centrifuged briefly to clarify, if necessary) and the colour is read in a 1-cm sample cell in a spectrophotometer at 520 $m\mu$, against a reagent blank treated in the same manner as the sample, 20 min. after the addition of the alcohol. The concn. of I can then be determined by comparison with a standard absorption curve, which is linear at concn. of I > 0.7 p.p.m.

S.C.I. ABSTR.

Agriculture and Plant Biochemistry

859. Spectrophotometric method for determining hydroxylamine reductase activity in higher plants. D. S. Frear and R. C. Burrell (Ohio State Univ., Columbus, U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1664-1665.—Hydroxylamine interacts quant. with an excess of 8-hydroxyquinoline to form the stable 5:8-quinolinequinone-5-(8-hydroxy-5-quinolyl-imine), which exhibits a prominent absorption peak at 705 $m\mu$. Beer's law holds at concn. up to 5×10^{-2} millimole per ml. Application to the determination of hydroxylamine reductase activity in soya-bean leaves was successful.

G. P. COOK

860. Differential colorimetry in a saline medium. Extension of the method to flavone derivatives. C. Mentzer and J. Jouanneteau (Fac. des Sci., Lyons, France). *Bull. Soc. Chim. Biol.*, 1955, **37** (7-8), 887-895.—The difficulty of differentiation, and at the same time determination, of two closely related substances can be overcome by increasing the specific differences by adding suitably chosen neutral salts, as described by Mentzer (*J. Pharm. Chim.*, 1938, **27**, 145) for determining glutathione in living tissues. The method has been extended to flavones and other natural constituents. Certain electrolytes may seriously affect the u.v. spectrum of substances and produce a new band or cause extinction of a characteristic max.; the extinction may also be changed. These facts may be used for differential determination of substances when paper chromatography fails.

P. HAAS

861. Saponins. VI. Analysis by partition chromatography. J. L. Fontañ-Candela. *An. Real. Soc. Esp. Fis. Quím.*, 1955, **51B**, 432-435.—Paper chromatograms are run at pH 1 and pH 7. The triterpenic saponins have R_F values twice as high at the lower pH, whereas steroid saponins, e.g., digitonin, show little change of R_F with pH. Information may be obtained in this way on the class of saponin in plant extracts, especially when considered in conjunction with the colour of the spot under ultra-violet light, which tends to appear blue with triterpenic and yellow with steroid saponins.

L. A. O'NEILL

862. Extraction and chemical determination of easily soluble boron, iron, cobalt, copper, manganese, molybdenum and zinc in soil. H. Baron (Land-

wirtsch. Versuchsants. Augustenberg, Germany). *Landwirtsch. Forsch.*, 1955, **7**, 82-89.—For the determination of easily soluble B, Fe, Co, Cu, Mn, Mo and Zn, 50 g of soil were extracted with a soln. of pH 4.0 made from ammonium acetate (20 g), $(NH_4)_2SO_4$ (66 g) and glacial acetic acid (62.5 g) diluted to 1 litre. The soln. was always saturated with respect to $CaSO_4$. The easily soluble B (0.1 to 15 p.p.m.) in the filtrate was determined with 1:1'-dianthrimide; Fe (5 to 100 p.p.m.) with $\alpha\alpha'$ -dipyridyl; and Mn (10 to 200 p.p.m.) as permanganate. Easily soluble Cu (0.3 to 6 p.p.m.) was determined with diethyldithiocarbamate; Co with 2-nitroso-1-naphthol; Mo (0.03 to 0.24 p.p.m.) with thiocyanate and $SnCl_2$; and Zn (0.5 to 10 p.p.m.) with dithizone.

CHEM. ABSTR.

863. Detection of NN'-diphenyl-p-phenylenediamine (DPPD) in dehydrated lucerne and in mixed feeds. H. Smith, R. E. Beauchene, D. B. Parrish and H. L. Mitchell (Kansas Agric. Exp. Stn., Manhattan, Kans., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (9), 788-789.—A simple and rapid specific test is described for the detection of NN'-diphenyl-p-phenylenediamine (I) in meal and mixed poultry feed. The test can detect ≈ 6 p.p.m. of I. *Procedure*—Activated magnesia (2 g) is stirred with 2 g of lucerne meal, or 10 g of mixed feed, in a mixture of hexane and acetone (1:1) (30 ml). The supernatant liquid is decanted and, if from lucerne meal, filtered, or, if from mixed feed, the treatment with magnesia is repeated before filtering. To the filtered extract, 5 ml of diluted HCl (1:3) and 1 drop of a 0.25 per cent. w/v soln. of $CuSO_4$ are added and the mixture is shaken. If I is present the aq. layer is blue to blue-green. The following test is more sensitive but less specific. Two drops of conc. HNO_3 are added to 10 to 20 drops of the filtered extract that have been evaporated almost to dryness. If I is present the soln. becomes blue and then red. "Santoquin" (6-ethoxy-1:2-dihydro-2:2:4-trimethylquinoline) gives similar colours.

S. C. JOLLY

864. Determination of the fluoride content of edible bone-meal. J. C. Bartlet, D. Kavanagh and R. A. Chapman (Dept. Nat. Hlth. and Welfare, Ottawa, Ontario, Canada). *Canad. J. Technol.*, 1955, **33** (5), 348-355.—The method described enables several hundred p.p.m. of F^- in edible bone-meal to be determined rapidly to ± 2.3 per cent., although it is not as sensitive as other colorimetric methods. *Procedure*—The sample (4 to 6 g) is ignited at 650° C for 2 hr., cooled and transferred to a 250-ml Claisen flask containing $HClO_4$ (30 ml), Ag_2SO_4 (0.2 g) and a small amount of sand. The fluorosilicic acid is distilled at 135° to 137° C according to the method of Churchill (*Brit. Abstr. C*, 1946, 79), and is collected in *N* NaOH soln. The distillate is made slightly acid with *N* $HClO_4$ and made up to 200 ml. A 5-ml aliquot is placed in a 25-ml calibrated flask, 1 ml of chloroacetic acid buffer (pH 3.1) and 5 ml of ferric salicylate soln. (Fe:salicylic acid = 0.404 by wt.) are added and the liquid is diluted to the mark. The extinction is then measured spectrophotometrically at 530 $m\mu$ in a 5-cm cell, with H_2O in the reference cell. The extinction of the sample is subtracted from the extinction of the blank, and the concn. of F^- is obtained from the calibration curve (0 to 120 μg of F^-). The aliquot should not contain $> 100 \mu g$ of F^- . Interfering ions (citrate, tartrate, PO_4^{3-} , SO_4^{2-} , Cl^- , Br^- , SO_3^{2-} , $S_2O_3^{2-}$, I^- , NO_2^- , Al^{3+} , Fe^{3+}) and

free Cl are almost completely eliminated by the distillation technique.

W. J. BAKER

865. Chemical determination of dieldrin in crop materials. A. E. O'Donnell, H. W. Johnson, jun., and F. T. Weiss (Shell Development Co., Emeryville, Calif., U.S.A.). *J. Agric. Food Chem.*, 1955, **3** (9), 757-762.—Two methods, based on those used for aldrin, are described for the determination of dieldrin residues on crops at concn. as low as 0.1 p.p.m. Both methods involve chromatographic separation of the pesticide from plant material, followed by determination either by (i) the combustion-Cl⁻ titration method (Agazzi *et al.*, *Brit. Abstr. C*, 1953, 367), or (ii) reduction of the epoxide group and determination of the partly dechlorinated aldrin formed by a modified phenyl azide spectrophotometric method (O'Donnell *et al.*, *Anal. Abstr.*, 1954, **1**, 2853). The latter method is more specific and sensitive.

S. C. JOLLY

866. Determination of nitrofurazone in mixed feeds. J. E. Dixon (J. Bibby & Sons, Ltd., Neston, England). *J. Sci. Food Agric.*, 1955, **6** (9), 556-558.—The method described is applicable to mixed poultry feeds. *Procedure*—The feed (1 g) is heated in a water bath, at about 80° C under a cold-finger condenser for 30 min., with 50 to 100 ml of light petroleum (boiling range, 80° to 100° C). The solvent is decanted through a sintered funnel (2.5 in. diam.), No. 3 porosity, and the residue is washed by decantation with two 20-ml portions of light petroleum (boiling range, 40° to 60° C). The petroleum extracts are rejected. The residue (still in the original flask) is dried for a few min. in an oven at 100° C, 50 ml of absolute ethanol are added, the flask is heated for 30 min. under the condenser and the soln. is filtered through the sintered funnel. The residue is washed twice with hot alcohol, and the combined filtrates are evaporated under reduced pressure to a volume of about 1 ml. The residue is quant. applied to a strip of Whatman paper No. 3 MM as a 4-in. streak by means of a capillary pipette; several applications are necessary, and the paper is dried between each in a stream of hot air without being overheated. The paper is run in chloroform-isopropyl alcohol-K benzoate solvent for about 4 hr. at room temp., the olive-green band of nitrofurazone is located, cut out, and extracted with boiling ethanol. The extract is evaporated to small vol. under reduced pressure, transferred quant. to a 10-ml calibrated flask, diluted to vol. with ethanol and measured at 365 m μ with the Uvispek spectrophotometer.

S.C.I. ABSTR.

867. Chromotropic acid method for determining 2:4-D residues in rinses. L. C. Erickson and B. L. Brannaman (Univ. Calif. Citrus Exp. Sta., Calif., U.S.A.). *Hilgardia*, 1954, **23**, 175-184.—The determination of 2:4-D (2:4-dichlorophenoxyacetic acid) by its conversion into formaldehyde and estimation of this colorimetrically with chromotropic acid is described. *Procedure*—Five ml of a standard or unknown 2:4-D soln. are transferred by pipette into an Erlenmeyer flask and the solvent is evaporated by blowing air into the gently heated flask; for esters of 2:4-D the heating is omitted. Five ml of conc. H₂SO₄ containing 50 mg of chromotropic acid are added to the residue, the flask then being heated at 130° C for 20 min. in an oil-bath. After the soln. has been cooled, the extinction at 580 m μ is measured in a spectrophotometer. The colour

was found to be stable for 9 days, but the chromotropic acid reagent was unstable and had to be prepared as needed. The ratio of chromotropic acid to 2:4-D must be > 25:1 and preferably 50:1. The colour development is incomplete at < 130° C (the optimum temp.), and the optimum time at this temp. is 20 to 40 min. Beer's law is obeyed over a wide range of concn. and under the conditions described the method is suitable for amounts of from 5 to 150 μ g of 2:4-D. At the minimum amount of 2:4-D, triplicate determinations on each of two samples showed that a difference of 1 mg per litre between samples was significant at the 5 per cent. level, and at the max. amount of 2:4-D this was 5 mg per litre.

T. G. MORRIS

868. Determination of salts of ethylenedis-dithiocarbamic acid in presence of copper salts in fungicides. P. Fontana and R. Martelli (Ist. di Chim. Agr., Univ. Cattolica del S. Cuore, Italy). *Ann. Fac. Agr. Univ. Cattol. S. Cuore*, 1955, **51**, Ser. 1, 187-191.—Organic matter is decomposed in the presence of ferrocyanide, which inactivates the Cu. A sample, containing 0.2 to 0.3 g of the ethylenedis-dithiocarbamate, together with about 1 g of K₄Fe(CN)₆, is digested with 50 ml of boiling 2 N H₂SO₄ for about 30 min. The first absorption vessel contains 25 ml of 15 per cent. Pb acetate, the second one 25 ml of methanolic KOH. Further details are those of the method originally suggested by Clarke *et al.* (*Brit. Abstr. C*, 1952, 225).

F. R. PAULSEN

See also Abstracts 651, 833, 834, 874.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

869. Recording micro-balance. A. H. Peterson (Mellon Inst. Ind. Res., U.S.A.). *Instrum. and Automation*, 1955, **28** (7), 1104-1106.—The iron core of a differential transformer hangs from the stirrup of a conventional analytical balance and is free to move within a ceramic cylinder on which are wound the three coils of a differential transformer. The primary winding is excited with a current of 60 c.p.s. and the iron core couples the two secondary coils, which are connected in opposition. Movement of the core increases the output of one of the secondary coils while decreasing that of the other. After conversion to direct current, the output is fed to a 1.0-mV recording potentiometer. By this means the sensitivity (10 mg per in. of pointer deflection) of the unmodified balance may be increased by a factor of more than 10,000.

G. SKIRROW

870. Temperature control of laboratory apparatus. II. K. A. Galloway (24, Apple Grove, Enfield, Middlesex, England). *Lab. Practice*, 1955, **4** (8), 334-338.—Methods are discussed for achieving the temp. control of certain laboratory apparatus, including hot-plates, muffle and tube furnaces, furnaces with controlled heating and cooling rates, ovens, incubators, water baths and humidity ovens.

J. H. WATON

871. Potentiometric method for Karl Fischer titrations. F. L. J. van Lamoen and H. Borsten (Vezelinstitut T.N.O., Delft, Netherlands). *Anal.*

Chem., 1955, **27** (10), 1638-1639.—When potentiometric titrations are carried out by the Karl Fischer - Johansson procedure, an accuracy equiv. to that found with the dead-stop technique can be attained with the use of two platinum electrodes and a pH meter. The bright-platinum reference electrode is placed in a tube containing the SO_2 -pyridine-methanol soln.; electrical contact with the soln. to be titrated is made through a thin asbestos-fibre sealed through the tube wall. The platinised-platinum indicator electrode is in a second glass tube perforated at the bottom. At the equiv. point, an e.m.f. change of ≈ 150 mV occurs.
W. J. BAKER

872. New hygrometer. L. Prins (Max-Planck-Institut für Strömungsforschung, Göttingen, Germany). *Kältetechnik*, 1955, **7** (9), 265-270.—An improved mirror hygrometer and its calibration are described. The mirror is cooled to a fixed temp. $> 0^\circ\text{C}$ to avoid ice formation; it is surrounded by an uncooled contrast mirror and is observed so that the image of a black surface is seen by regular reflection, but diffuse reflection of a lamp beam is seen when dew is deposited. The air under test is forced over the mirror at ≈ 5 metres per sec. by a compressor, and the total pressure is regulated by a needle valve, whereby its values at the appearance and disappearance of dew are closely adjustable. The results agree well with those from gravimetric determinations of moisture content. The precision is within ± 1 per cent., even at low dew-points.
A. R. PEARSON

873. Apparatus for measuring the rate of flow of solutions in laboratory chromatographic columns. K. V. Chmutov, T. B. Gapon and M. D. Yudilevich (Inst. Phys. Chem., Acad. Sci., Moscow). *Zavod. Lab.*, 1955, **21** (5), 627-628.—Continuous registering of rates of flow of liquids in chromatographic columns over the range 1 to 50 ml per min. is effected by means of a simple home-made rotameter, the construction of which is described and illustrated.
G. S. SMITH

874. Digester and filter for preparing extract solutions from solids. G. R. Van Atta and J. Guggolz (Agric. Res. Service, U.S. Dept. Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1669-1670.—The all-glass apparatus described and illustrated can be used for repeated extractions of macro amounts of plant materials with fresh vol. of solvent or reagent. The device is made by sealing a Büchner glass-funnel (fitted with a coarse fritted disc) to a spherical flask (300 to 3000 ml) and ensuring connections to a cold-finger condenser and a suitable receiver. Two glass caps are provided for prolonged extractions at room temp.
W. J. BAKER

875. Automatic apparatus for fluoride distillation. W. B. Estill and L. C. Mosier (Ozark-Mahoning Co., Tulsa, Okla., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1669.—In the apparatus described and shown, fluoride-distillation difficulties have been almost completely eliminated by keeping the liquid level low in the distilling flask, maintaining close control of temp. (to $\pm 1^\circ$ at 135°C) with a glass-enclosed thermostat connected in series with the heating coil, and by minor features of construction.
W. J. BAKER

876. Fraction collector for chromatography. E. T. Sanders (Unilever Ltd., Port Sunlight, Ches., England). *J. Sci. Instrum.*, 1955, **32** (10), 392-393.—The instrument comprises a balance that collects and delivers equal fractions alternately to each of two receivers, which collect the fractions and deliver them to sample tubes mounted on a motor-driven turn-table.
G. SKIRROW

877. New technique in ion-exchange chromatography. D. K. Hale (Chem. Res. Lab., D.S.I.R., Teddington, Middlesex, England). *Chem. & Ind.*, 1955, (37), 1147-1148.—A Whatman No. 1 filter-paper was disintegrated in water (6 g in 500 ml) with a laboratory blender and mixed with wet Zeo-Karb 225, or Amberlite IRA-400 (20 g), with stirring. The mixture was ball-milled for 30 min., diluted (to 4 litres) with de-ionised water and the suspension poured on to a fine filter-cloth in a Büchner funnel (or a wooden tray with a perforated metal base). The re-formed filter-paper was then dried and used in a number of chromatographic separations, e.g., Cu and Cd, Pr and Nd (partial), Co and Ni, and chlorides, bromides and iodides.
S.C.I. ABSTR.

878. A broad-range viscometer. Z. Večeřa (Považské chemické závody, Žilina, Czechoslovakia). *Chem. Listy*, 1954, **48** (10), 1574.—The Ubbelohde viscometer, modified by the addition of a second capillary of different diameter, is described, and tested by measuring the changes in viscosity of methylated caprolactam during polymerisation in the bulb of the instrument. The measured viscosity ranges from 1 to 1300 centipoises.
G. GLASER

879. A new type of osmometer for aqueous solutions. J. L. Gardon and S. G. Mason (McGill Univ., Montreal, Que., Canada). *Canad. J. Chem.*, 1955, **33** (9), 1453-1458.—The construction and operation of the osmometer are described. The membrane is held by dental dam gaskets between two stainless-steel screens to prevent ballooning. The screens are held by rubber rings against two Lucite discs, with inlet holes, the whole being clamped together between two brass rings. The cell chambers between the Lucite and the screens are packed with glass rods to reduce their capacity. Separable (spherical ground-glass joints) toluene manometers are used, with a glass syringe for levelling. Advantages are avoidance of metal surfaces which trap air bubbles, reduction in capillarity errors in the manometer, large membrane area with avoidance of ballooning, small cell capacity, transparency of unit and changeability of solutions without dismantling.
A. B. DENSHAM

880. Modified Ramsey-Young apparatus for measuring vapour pressures of liquids. W. H. Dumke. *J. Chem. Educ.*, 1955, **32** (7), 383.—Details are given for the construction and use of a modified apparatus whose chief advantages are ensured uniform flow of drops, more accurate pressure readings and greater durability of the apparatus.
A. LEDWITH

Optical

881. Use of a reflectance attachment to obtain excitation spectra. C. A. Lermond and L. B. Rogers (Mass. Inst. Tech., Cambridge, Mass., U.S.A.). *Anal. Chim. Acta*, 1955, **13** (4), 387-392.—The Beckman DU spectrophotometer with reflectance attachment is used to obtain excitation spectra of fluorescent substances. The reflectance attachment consists of a mirror and a lens which direct the light from the sample to the photometer cell. The mirror is mounted on a rotating turntable which can be rotated through 360° . The lens is mounted on a sliding support which can be moved along the turntable. The distance between the mirror and the lens is adjustable. The reflectance attachment is used to measure the reflectance of a sample at a given wavelength. The reflectance is then used to calculate the excitation spectrum of the sample.

tance attachment and certain modifications is used to determine the excitation spectrum of dichlorofluorescein. It is shown that emittance measurements can be used to determine low concn. of fluorescent substances. A differential technique is proposed for the study of self-absorption and quenching effects. By plotting the emittance against the wavelength and comparing the curve with standards prepared from the pure substances it is possible to detect fluorescein derivatives in the presence of one another, e.g., dichlorofluorescein in fluorescein.

W. C. JOHNSON

882. New recording spectrophotometer. B. S. Pritchard and W. A. Holmwood (General Electric Company, Schenectady, New York). *J. Opt. Soc. Amer.*, 1955, **45** (9), 690-695.—The various design features of the new version of the General Electric recording spectrophotometer are described. New slit arrangements on the monochromator have doubled the light transmission of the instrument. With the new servo system the speed has been increased; the didymium curve can be plotted from 380 to 700 m μ in less than one minute. As with the earlier model, the instrument can be used for either spectral transmission or spectral reflection measurements.

B. S. COOPER

883. Cyanogen-oxygen flame as a spectrochemical source. M. R. Baker and B. L. Vallee (Harvard Medical School, U.S.A.). *J. Opt. Soc. Amer.*, 1955, **45** (9), 773.—The temperature of the (CN)₂-O flame is among the highest produced by any chemical reaction (about 4700° K), and this source is therefore capable of exciting the spectra of many elements whose excitation potential is too high for excitation by the more conventional sources used in flame photometry, such as the oxy-hydrogen flame. Preliminary investigations show that the line spectra of Ag, Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Sr are readily excited in the (CN)₂-O flame and can be detected under conditions which indicate that the spectrographic sensitivities are approximately equal to, and may even exceed, those in the d.c. arc. Under otherwise identical conditions, no spectral lines of any of the elements listed were observed in the oxy-hydrogen flame.

B. S. COOPER

884. Furnace for obtaining optical spectra of radioactive elements. L. F. H. Bovey (Atomic Energy Research Estab., Harwell, England). *J. Sci. Instrum.*, 1955, **32** (10), 376-378.—Constructional and operational details of a King-type furnace (a carbon tube heated by the passage of large currents) are described. The furnace has been used for the examination of the absorption spectra of Sc, Y and La. Both emission and absorption spectra of U and Pu have been observed within the range 2400 to 7000 Å in the second order of a 3-metre-grating spectrograph.

G. SKIRROW

885. A micro-cuvette designed for absorption measurements of biological fluids with high density values. S. E. Brolin (Uppsala Univ., Sweden). *Acta Physiol. Scand.*, 1955, **33** (4), 371-372.—The design of cuvettes of methyl methacrylate resin for measuring the absorption of small samples of biological fluids with high density values is given. When calibration was performed by using a pair of cuvettes filled with distilled water, the error of the density values was less than 0.5 per cent. in most of the spectral regions.

O. M. WHITTON

886. Near-infra-red spectroscopy. II. Instrumentation and technique. A review. W. Kaye (Eastman Kodak Co., Kingsport, Tenn., U.S.A.). *Spectrochim. Acta*, 1955, **7** (4), 181-204.—In a comprehensive review the author deals with optical materials, gratings, multi-pass operation, detectors, cells, sources, filters, recording, sample handling, slit-width effects, stray light, polarisers, micro-spectroscopy and calibration. (242 references.)

K. A. PROCTOR

887. Devices for analysis of the refractive indices of solutions. Sandoz Ltd. (35, Lichtstr., Basle, Switzerland). Brit. Pat. 736,259; Date Appl. 15.7.53.—The device, which is adapted to record, in rapid succession on the same x-scale, the changes in refractive index as a function of distance (n/x diagram) and the derivative of the refractive index with respect to the same distance ($\frac{dn}{dx}$ diagram),

has an optical system provided with interchangeable components, mounted on turn-tables and operated by interconnected rods, whereby a set of components for recording the refractive index gradients can be interchanged (and automatically centred and focused) with another set for recording the changes in the gradients. The two recordings are thus produced at the same position and can be superimposed.

J. M. JACOBS

888. Simple photo-electric polarimeter. T. B. Crumpler, W. H. Dyre and A. Spell (Tulane Univ., New Orleans, La., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1645-1648.—With the arrangement described by Landt and Hirschmueller (*Dtsch. Zuckerind.*, 1937, **62**, 646), a photo-electric colorimeter can be converted into a two-photocell polarimeter that eliminates the need for an angular scale and has a fixed polariser and moveable analyser, both of Polaroid. The angle of rotation is calculated from successive readings of transmittance values. The reproducibility of rotation measurements is $\approx 0.03^\circ$. The mean correction factor is 1.026.

W. J. BAKER

Thermal

889. New procedure for the melting-point determination of macromolecular substances. F. Rybníkář (Výzkumný ústav pro využití plastických hmot, Gottwaldov, Czechoslovakia). *Chem. Listy*, 1954, **48** (10), 1575-1576.—A simply constructed apparatus, in which the sample and the thermometer are directly immersed in mercury contained inside a glass-tube reservoir, is described and illustrated. It is especially suitable for determining the melting-, or softening-point of macromolecular compounds. The results are somewhat higher than those obtained by current methods.

G. GLASER

890. New method for melting-point determination. M. A. Phillips. *Chem. Prod.*, 1955, **18** (9), 347.—A melting-point determination apparatus consists of a copper block with apertures for the thermometer and melting-point capillary or capillaries, an inspection hole at right-angles to the melting-point capillary tube, a rod for support in an ordinary laboratory clamp and retort stand, and a copper heating rod along which a temp. gradient can be formed by heating with a micro-burner.

I. JONES

891. Simplified apparatus and procedure for freezing-point determinations upon small volumes of fluid. J. A. Ramsay and R. H. J. Brown (Zool. Lab., Univ. Cambridge). *J. Sci. Instrum.*, 1955, **32** (10), 372-375.—Small samples (10^{-3} to 10^{-4} cu. mm) of aqueous solutions contained in glass capillaries are frozen and the thawing-points are observed as the ambient temp. is slowly raised. An accuracy of $\pm 0.003^\circ\text{C}$ for freezing-point depressions of 1° to 2°C is claimed.

G. SKIRROW

Electrical

892. Dynamic capacitor modulator for use in electrometer [amplifiers, particularly for the measurement of hydrogen-ion concentration]. Beckman Instruments, Inc. (820 Mission St., South Pasadena, Calif., U.S.A.). Brit. Pat. 732,995; Date Appl. 13.11.52.—A modulator adapted to receive a d.c. or slowly varying input signal and produce an a.c. output signal which varies with changes in magnitude of the input signal, comprises a tubular glass envelope wherein are resiliently mounted a pair of sheet-metal plates with closely spaced, electrically conductive surfaces forming a capacitor. An electromagnetic coil surrounding the envelope in the region of the plates induces a magnetic-flux change of like polarity along similarly oriented magnetic axes in both the plates, and a relative vibrating motion is set up by variations in mutual repulsion between the plates when the coil is energised by an a.c. current. The output signal, which is produced at a multiple of the frequency of the a.c. source, is amplified and the output from the amplifier is converted to a d.c. output by a synchronous demodulator to provide a measure of the input signal.

J. M. JACOBS

893. Automatic coulometric titrations involving an amperometric end-point. H. L. Richter, jun. (Calif. Inst. Technol., Pasadena, Calif., U.S.A.). *Anal. Chem.*, 1955, **27** (10), 1526-1531.—An instrument for the automatic control of a coulometric titration by means of the dual-indicator-electrode amperometric end-point is described and illustrated. The titration is stopped at a pre-set indicator current, either as a dead-stop end-point or as a preliminary operation to the calculation of the exact end-point by extrapolation. The circuit diagram is shown and the operation of the instrument on the following different amperometric end-points is described: (i) titration of Sb^{+++} with electrolytically generated Br, (ii) titration of $\text{S}_2\text{O}_8^{--}$ with electrolytically generated I, and (iii) titration of I^- with electrolytically generated Br. The error for (i) is ≈ 0.2 per cent.; the accuracy and reproducibility for (ii) and (iii) are satisfactory.

W. J. BAKER

894. A correlation chart for solution concentrations measured by circuits whose constants are not in agreement. G. G. Blake (Univ. of Sydney, Australia). *Anal. Chim. Acta*, 1955, **13** (4), 393-395.—The chart relates the respective micro-

ammeter deflections obtained in the determination of soln. concn. by radio-frequency and low-frequency methods, and relates these measurements to the known resistance of standard solutions.

W. C. JOHNSON

895. An electromagnetic stirring device for Warburg manometers. Bal Krishna and M. Sreenivasaya (Central Drug Research Inst., Lucknow, India). *J. Sci. Ind. Res., B, India*, 1955, **14** (8), 425-426.—An electromagnetic stirring device for Warburg manometers is illustrated and described. The device obviates (1) risk of breakage when both the amplitude and the frequency of the oscillations have to be increased and (2) the necessity of arresting the shaking mechanism to take readings.

I. JONES

896. Flow-through measuring cell for the Karl Fischer titration by the end-stop method. H. Praeger. *Chem. Tech., Berlin*, 1955, **7** (8), 480.—The cell described for use in the Karl Fischer titration (for estimating the water content of org. or inorg. compounds and estimating functional groups) avoids the use of a fresh dry measuring vessel for each titration and expedites determinations in a series of analyses. The cell has two platinum electrodes, the one over the other, and the sample solution is introduced at a point between the electrodes by a side tube in the cell. This side tube has a ground mouth for connection to a tube of P_2O_5 during titration. The base of the cell is provided with a rubber stopper, double-bored for the introduction of a stirrer and the burette connection. A glass tap at the base of the cell enables the solution to be drained off after titration. For samples of low water content, 2 ml of the sample are added to the cell by pipette and are titrated with the Karl Fischer solution, with vigorous stirring, to the requisite deflection on the measuring instrument. For samples of higher water-content, portions are weighed and made up to 10 ml, and 2 ml of the diluted sample are titrated. Standardisation is effected with standard aq. methanol (0.5 g of H_2O in 100 ml).

H. L. WHITEHEAD

897. Apparatus for defining the percentage of moisture contained in relatively electrically non-conducting materials [textiles, plastics, tobacco, etc.]. H. Eicken, generally known as Estienne (60 Boulevard des Belges, Lyons, France). Brit. Pat. 737,145; Date Appl. 8.7.53.—A voltage of one polarity (negative bias) is applied to the control grid of a thermionic valve through a capacitive resistance, and a rectified pulsating voltage of opposite polarity is applied to the grid through two electrode feelers engaging the material under test, the feeler that is most remote from the grid in the grid circuit being earthed. The moisture content of the material affects the operative point on the potential curve of the control grid, resulting in a modification of the anode current of the valve, which is indicated on a galvanometer.

J. M. JACOBS

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use in the text of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	millicurie	mC
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicron	mμ
aqueous	aq.	millivolt	mV
atmosphere, -e, -ic	atm.	minimum	min.
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecule, -e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	number	no.
coefficient	coeff.	observed	(obs.)
concentrated	conc.	ounce	oz
concentration	concn.	part	pt.
critical	crit.	patent	pat.
crystalline	{ cryst.	parts per million	p.p.m.
crystallised	{	per cent. wt. in wt.	per cent. w/w
cubic	cu.	per cent. wt. in vol.	per cent. w/v
current density	c.d.	per cent. vol. in vol.	per cent. v/v
cycles per second	c.p.s.	potential difference	p.d.
decomposition, -ing, -ition	(decomp.)	pound	lb
density	ρ	precipitate	ppt.
density, relative	d or wt. per ml	precipitated	pptd.
derivative	deriv.	precipitating	pptg.
dilute	dil.	precipitation	pptn.
direct current	d.c.	preparation	prep.
distilled	dist.	qualitative, -ly	qual.
electromotive force	e.m.f.	quantitative, -ly	quant.
electron-volt	eV	recrystallised	recryst.
equivalent	equiv.	refractive index	n _D
experiment	expt.	relative humidity	R.H.
foot, feet	ft.	revolutions per minute	r.p.m.
gram	g	saponification value	sap. val.
gram-molecule	mole	saturated calomel electrode	S.C.E.
half-wave potential	E _{1/2}	second (time)	sec.
horse-power	h.p.	soluble	sol.
hour	hr.	solution	soln.
hydrogen ion concentration [H ⁺]	[H ⁺]	specific gravity	sp. gr.
hydrogen ion exponent	pH	specific rotation	[α] _D
inch	in.	square centimetre	sq. cm
infra-red	i.r.	standard temperature and pressure	s.t.p.
insoluble	insol.	temperature	temp.
kilogram	kg	ultra-violet	u.v.
kilovolt	kV	vapour density	v.d.
kilowatt	kW	vapour pressure	v.p.
maximum, -um, -a	max.	volt	V
melting-point	m.p.	volume	vol.
microcurie	μC	watt	W
microgram	μg	wavelength	λ
microlitre	μl	weight	wt.
micron	μ		
milliamperes	mA		

In addition the following symbols are used—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P., or D.A.B., together with the identifying numeral.

Radicals are represented by the usual symbols; positive ions have superscript dots and negative ions superscript dashes, e.g., Cu⁺⁺, Al⁺⁺⁺, Cl⁻, SO₄⁻². Metals that exist in more than one valency state are represented by their symbols with appropriate superscript roman numerals, e.g., ferric iron becomes Fe^{III} and cuprous copper Cu^I.

ANALYTICAL ABSTRACTS

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CONTENTS

	Abstract
General Analytical Chemistry	625
Inorganic Analysis	641
Organic Analysis	733
Biochemistry	
Blood, Bile, Urine, etc.	778
Drugs	805
Food	833
Sanitation	855
Agriculture and Plant Biochemistry	859
General Technique and Laboratory Apparatus	
General	869
Optical	881
Thermal	889
Electrical	892

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